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The Quenching of Mercury Resonance Radiation by Compounds Containing Deuterium

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The quenching of mercury resonance radiation by hydrogen, deuterium, ammonia, deuteroammonia, water vapor and heavy water vapor has been measured. It has been possible to correlate the differences in quenching efficiencies between the heavy and ordinary compounds with the changes in the vibrational level of the molecules which are brought about by the introduction of deuterium atoms. The quenching cross sections obtained fall on the general type of resonance curve.

THE problem of the transfer of energy between colliding particles is of fundamental importance in the physical chemistry of kinetics. The problem of quenching of resonance radiation by small amounts of foreign gases is a special case of the more general problem of energy transfer. In this case the transfer of energy is one in which energy of excitation may be transferred to the foreign gas molecule either as energy of excitation, or as vibrational energy, and the chemist has been interested in the reactions which molecules undergo subsequent to this transfer of energy. The discovery of the heavy isotope of hydrogen and the formation of compounds in which this isotope is substituted for ordinary hydrogen has given the chemist a means of studying the mechanism of a number of reactions in which hydrogen and its compounds take part. It was the purpose of this research to discover if possible whether the definite changes one could make by the substitution of deuterium for hydrogen would profoundly affect the nature and efficiency of processes involving an exchange of energy, and this special case of energy exchange was chosen as one affording the most direct method of attack. Further the author had previously carried out an investigation of the rate of the photosensitized reaction between deuterium and oxygen, and for comparison of these results with those obtained for hydrogen and oxygen, it was necessary to know whether there was a difference in the efficiency of hydrogen and deuterium in quenching mercury resonance radiation.

EXPERIMENTAL PROCEDURE

The experimental method employed was similar to that used by Zemansky[1] and by Bates,[2] full experimental details being given in their publications. The source of mercury resonance radiation used to illuminate the resonance lamp was a Hanovia resonance arc; spectroscopic examination of the light from this source showed it to be very rich in the 2537 line.

The intensities of the resonance radiation were

[1] Zemansky, Phys. Rev. **36**, 919 (1930).
Mitchell and Zemansky, Resonance Radiation and Excited Atoms, Macmillan Co., 1934.

[2] Bates, J. Am. Chem. Soc. **52**, 3825 (1930); **54**, 569 (1932).

measured by means of a platinum photoelectric cell constructed in the manner described by Zemansky, and the photoelectric currents were measured by means of a sensitive Compton electrometer.

The quenching Q is expressed as the intensity of resonance light emitted in the presence of a definite pressure of foreign gas divided by the intensity of emitted resonance radiation at zero foreign gas pressure

$$Q = I_{\text{R.p.}}/I_{\text{R.vac.}} \times 100.$$

Preparation of gases and vapors used

Hydrogen was prepared by the electrolysis of caustic potash solution, the oxygen and hydrogen being evolved in separate compartments. The hydrogen so formed was passed over a drying train of phosphorus pentoxide and then over heated platinized asbestos to remove traces of oxygen. The gas was then passed through a U-tube packed with charcoal (activated *in situ*) and cooled in liquid air; finally the gas was further dried by passing over phosphorus pentoxide and stored in a glass bulb from which it was admitted into the quenching apparatus.

Deuterium was prepared in a similar way by the electrolysis of 100 percent heavy water, the purification train being, apart from the U-tube of active charcoal, of the same kind as that used for ordinary hydrogen. Ammonia was prepared by the action of caustic potash on synthetic ammonium chloride, the gas being dried first by solid caustic potash, and lime, and finally after repeated condensation and fractional distillation the gas was condensed over phosphorus pentoxide which had been freshly distilled in a stream of oxygen *in situ*, and then was allowed to evaporate into an evacuated bulb in which the gas was stored.

The deutero-ammonia was loaned by Professor Hugh S. Taylor and Dr. J. C. Jungers and had been prepared in the manner described by them.[3] The heavy water used contained 100 percent deuterium and had a density of 1.1059 at 20°C.[4] The electrical conductivity of the water was 3×10^{-6}.

Gas pressures were measured by means of a McLeod gauge and the water vapor pressures were maintained constant by means of constant temperature baths. The data given by Lewis[5] for the vapor pressure of heavy water at various temperatures were used to calculate the pressures of heavy water vapor in the apparatus.

Experimental Results

Zemansky,[1] employing Milne's theory, has developed an expression for the intensity of scattered radiation emerging from unit area of the face of the absorption cell next to the photoelectric cell. The intensity is given by

$$\pi I_+ = KG(kl, \tau Z_Q),$$

where K is the intensity of the collimated beam and G depends on only two quantities kl, where k is the absorption coefficient of the gas in cm^{-1} for the radiation in question, and l the thickness of the absorption cell; and on τZ_Q where τ is the mean life of the excited mercury atom in the $^3P_1$ state and Z_Q is the number of collisions between foreign gas molecules and excited mercury atoms which are effective in bringing about quenching. From a knowledge of $k(\nu)l$ it is possible to obtain a relationship between the quenching Q and the quantity τZ_Q. Fig. 1 shows

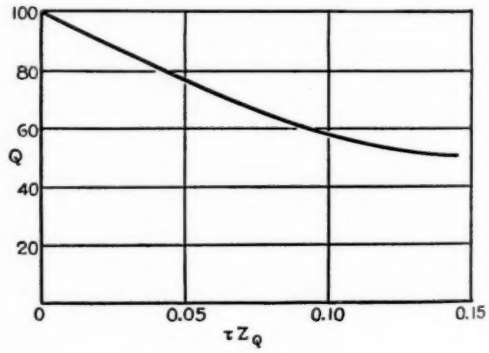

FIG. 1.

graphically the relationship between Q and τZ_Q which was used in these experiments. The results of the experimental work are tabulated in Table I and values of Q (the quenching) are plotted against p in Fig. 2. Table II gives the values of the quenching cross section σ_Q^2 cal-

[3] Taylor and Jungers, J. Am. Chem. Soc. **55**, 5057 (1933).
[4] Taylor and Selwood, J. Am. Chem. Soc. **56**, 998 (1934).
[5] Lewis and Macdonald, J. Am. Chem. Soc. **55**, 3057 (1933).

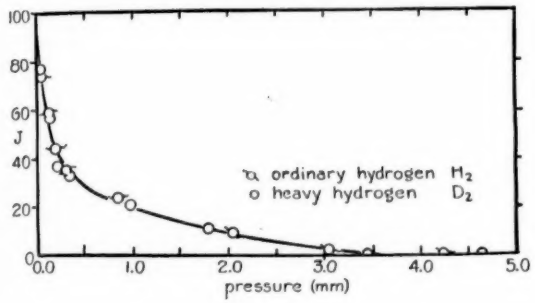

FIG. 2a.

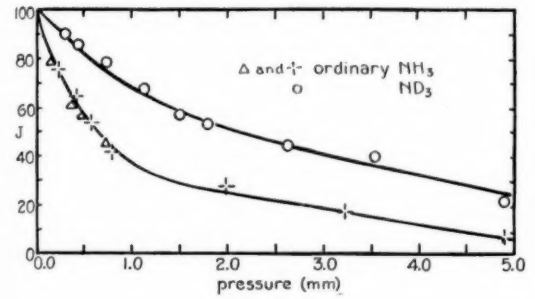

FIG. 2b.

culated from the slopes of the lines obtained by plotting τZ_Q against p and in the case of hydrogen and ammonia good agreement is obtained with the values for these gases determined by Zemansky. Fig. 3 shows the relationship τZ_Q against p. The values for deutero-ammonia and for heavy water vapor fall well below the values obtained for the ordinary compounds. The compounds containing the deuterium being in both cases very much less efficient than the ordinary compounds in quenching mercury resonance radiation. The difference between the heavy and the light compounds is one which is not merely due to the difference in mass, and hence due to the total number of collisions, but, as is seen from the values of the cross sections of

TABLE I.

Hydrogen Pressure in mm	Q	*Deuterium* Pressure in mm	Q	*Ammonia* Pressure in mm	Q	*Deutero-ammonia* Pressure in mm	Q
0.04	77.0	0.05	74.1	0.16	78.0	0.31	90.0
0.13	58.9	0.12	57.0	0.23	75.1	0.44	85.4
0.22	37.0	0.19	44.3	0.43	64.8	0.72	78.1
0.34	33.1	0.31	35.2	0.49	56.5	1.13	67.2
0.98	21.1	0.84	24.0	0.58	53.4	1.49	56.5
				0.75	45.0	1.79	53.1
				0.80	41.8		

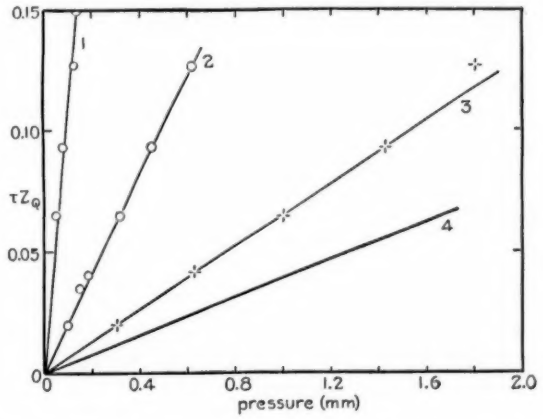

FIG. 3. (1) Hydrogen and deuterium; (2) ammonia; (3) deutero-ammonia; (4) heavy water.

quenching σ_Q^2, where the difference in mass has been taken into account, this difference persists and is due to definite changes in the molecule brought about by the introduction of deuterium atoms.

Deuterium itself on the other hand is within the experimental error of this work equally as efficient as hydrogen in quenching mercury resonance radiation. The values of the quenching obtained for hydrogen and deuterium at various pressures lie practically on the same curve; if a distinction could be made one would say that deuterium showed slightly better quenching than hydrogen.

This result is in accordance with the author's work on the rate of the photosensitized reaction between oxygen and hydrogen or deuterium, and further, some preliminary experiments of Taylor and Jungers have shown that hydrogen and deuterium have apparently the same effect in retarding the rate of photosensitized decomposition of ammonia. Although both these gases give apparently the same $\tau Z_Q/p$ values because

TABLE II.

Gas	$\tau Z_Q/p$	σ_Q^2 $\times 10^{-16}$	Normal σ^2 $\times 10^{-16}$	ΔE volts	E volts
Hydrogen H_2	1.08	6.01	8.89	4.46	4.86
Deuterium D_2	1.08	8.41	8.89	4.54	4.86
Ammonia NH_3	0.200	2.94	10.8	0.202	0.218
		3.04			
Deutero-ammonia ND_3	0.065	1.09	10.8	0.29	0.218
Water vapor H_2O	0.064	1.00	10.0	0.197	0.218
Heavy water vapor D_2O	0.038	0.46	10.0	0.15	0.218

of the difference in mass between hydrogen and deuterium the quenching cross section of deuterium is greater than that of hydrogen.

Theoretical Discussion

The quantum-mechanical considerations[6] of the problem of the transfer of energy are too general in nature to be applicable quantitatively to any special cases involving relatively complex molecules. There are, however, broad generalizations which emerge from the theoretical treatment.

The efficiency of the process of transfer of energy depends upon the relative positions of the energy levels in the colliding particles, that is on the energy which the excited atom is able to give, and the energy which the colliding molecule is able to receive, either as energy of excitation or as vibrational energy. Any excess energy or deficiency of energy transferred must be adjusted by an adjustment of the kinetic energy of the particles before and after collision. So that the less energy which it is necessary to transfer into kinetic energy, the more efficient will be the transfer of energy.

In the case of excited mercury it is possible that the quenching process may be one of two kinds. The mercury excited to the $^3P_1$ state may by collision with a molecule be degraded to the $^1S_0$ ground state, a process which would involve the transfer of 4.86 volts; or on the other hand the mercury may be "quenched" to the metastable $^3P_0$ state a change involving only 0.218 volt.

In the case of hydrogen it is very evident that the collision is one in which the whole of the energy of full excitation is transferred to the hydrogen, and during or subsequent to this collision the hydrogen is dissociated as a result of the transfer of energy. The dissociation of the hydrogen would involve 4.46 volts. There is, however, abundant spectroscopic evidence for the formation of mercury hydride HgH from hydrogen and mercury when photosensitized by the mercury resonance line. Beutler and Rabinowitsch[7] have found that in the HgH band, which appears when mercury and hydrogen are illuminated with mercury resonance light, the high rotational states of HgH are very intense. This observation being in agreement with their theoretical conclusion that, if during a collision of the type $A'+BC\rightarrow(AB)^{rot}+C$, A is an atom of large mass, AB will possess after the collision a large amount of rotational energy. Both the processes suggested for the quenching of excited mercury by hydrogen are energetically possible, and moreover, obey Wigner's[8] rule for conservation of total spin momentum during the process

$$\underset{1}{\mathrm{Hg}}(^3P_1)+\underset{0}{\mathrm{H_2}}(^1\Sigma)\rightarrow \underset{0}{\mathrm{Hg}}(^1S_0)+\underset{\frac{1}{2}}{\mathrm{H}}(^2S)+\underset{\frac{1}{2}}{\mathrm{H}}(^2S)$$

$$\underset{1}{\mathrm{Hg}}(^3P_1)+\underset{0}{\mathrm{H_2}}(^1\Sigma)\rightarrow \underset{\frac{1}{2}}{\mathrm{HgH}}(^2\Pi)+\underset{\frac{1}{2}}{\mathrm{H}}(^2S).$$

It was with the hope that any differences between the efficiencies of deuterium and ordinary hydrogen in quenching excited mercury would give an indication of the mechanism of the process, that the quenching of both hydrogen and deuterium was determined. The collision between an excited mercury atom and a hydrogen molecule and the transfer of excitation energy during this collision may raise the vibrational level of the hydrogen molecule to a level near or above the dissociation level, and in this region the vibrational levels of the hydrogen will be so close together that there will be no difficulty in finding a level which will give an exact correspondence in energy. In other words the transfer of 4.86 volts to the hydrogen will always raise the vibrational level into the continuum where the molecule will always have a vibrational level demanding the exact energy transfer. This, however, would necessitate that the excess energy over that required for dissociation would be accommodated as kinetic energy in the resultant particles and we have stated that the smaller the amount of energy it is necessary to transfer into kinetic energy, the more efficient will be the process of energy transfer. Because of the smaller zero point energy of deuterium the

[6] Kallman and London, Zeits. f. physik. Chemie **B2**, 207 (1929).

[7] Beutler and Rabinowitsch, Zeits. f. physik. Chemie **B8**, 231, 403 (1930).

[8] Wigner, Nachr. Götting. Ges. 375 (1927).

energy of dissociation of the deuterium molecule will be greater than for the hydrogen molecule, and hence, in the case of deuterium, there will be a closer correspondence between the energy transferred from the excited mercury atom, and the energy which the molecule can take up. Hence in the case of deuterium molecule we should expect on this basis a larger quenching cross section than in the case of hydrogen.

If on the other hand the hydride or deuteride of mercury is formed during the process, then, in considering the energy change, not only will the zero point energy difference of the hydrogen and deuterium have to be taken into account, but also the zero point energy difference for mercury hydride and mercury deuteride in the $^2\Pi$ state. Such a mechanism will naturally diminish the difference between the energies of the two processes with hydrogen and deuterium. Moreover, as has been shown by Rabinowitsch and Beutler the mercury hydride formed will be in a high rotational level and the corresponding compound with deuterium will possess a larger moment of inertia, since in the deuterium compound the center of gravity will not be greatly altered, because of the large mass of the mercury, while the mass of the revolving deuterium particle has been doubled.

The other compounds which have been studied are generally supposed to bring about the transition $^3P_1 \rightarrow {}^3P_0$ in the excited mercury atom. This is a process which involves an energy change of 0.218 volt and this amount of energy is taken up by the colliding molecule in the form of vibrational energy. That this process is not the only one which occurs is evident from the chemical reactions which occur when water vapor and ammonia are illuminated, in the presence of mercury vapor, by mercury resonance light, since the transfer of 0.218 volt is totally inadequate to bring about such chemical decomposition. Several workers have, however, supposed that ammonia and water vapor along with carbon monoxide, nitrogen, carbon dioxide, methane and nitric oxide, are effective in causing predominantly the transition of excited mercury from the $^3P_1$ to the metastable $^3P_0$ state, and we shall for the purpose of this discussion adhere to this viewpoint.

It became very evident from the theoretical work of Morse and Stueckelberg[9] that the form of resonance curve obtained by plotting the quenching cross sections against the energy difference between the levels of the colliding particles, was dependent upon the nature of the interaction between the particles. The use of different potential fields between the colliding particles led to different forms of resonance curve. Furthermore, these workers found that the sharpness of the resonance curve is greater in large molecules, and undoubtedly, as pointed out by Bates when discussing the relative quenching cross sections of butane and heptane, the shape and steric configuration of the molecules probably play a large rôle in determining the efficiency of quenching. Having these considerations in mind a resonance curve made up of quenching cross sections of a variety of molecules can do little more than indicate that the general form of such a curve is obeyed, and a number of factors may very well enter in causing erratic variations from one molecule to another.

In molecules in which ordinary hydrogen atoms can be replaced by deuterium atoms, we have a method of changing the vibrational levels and the mass of the molecule in a well-defined way, and it is probable that in so doing we are not bringing about very profound changes in the nature of the potential field which would affect the quenching cross sections so that we are able to vary the energy levels of the molecules in such a way as to give more significance to comparisons of quenching cross sections.

Let us consider the changes in the vibrational energy levels of ammonia as we successively replace the hydrogen by deuterium. The vibrational levels of ammonia and the various deuterium substituted ammonias are shown in Fig. 4 (a) and Table III. The dotted line in the

TABLE III.

	ν_1	ν_2	ν_3 cm^{-1}
Ammonia	938	1631	3336
Deutero-ammonia	770	1158	2421
Water	1615	3670	3795
Heavy water	1216	2670	2782

[9] Morse and Stueckelberg, Ann. d. Physik [5] 9, 579 (1931).

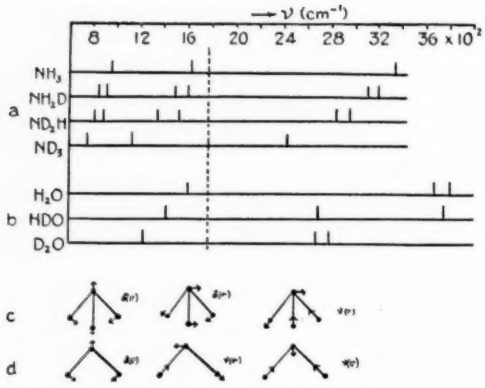

FIG. 4.

figure represents in comparable units, the energy given to the ammonia by the $^3P_1 \rightarrow {}^3P_0$ mercury transition, namely 0.218 volt. In the case of ordinary ammonia the vibrational level at 1679 is the one lying nearest to the energy of 0.218 volt, and in quenching mercury to the metastable state it is probable that this level is responsible, and that after a successful quenching collision the ammonia molecule will have been raised to this vibrational state from the ground state.

When a deuterium atom is substituted in ammonia each of the degenerate vibrational levels now breaks up into two non-degenerate levels, since the symmetry of the molecule has been destroyed. These new levels are not as yet known but it is possible to assess roughly their positions as in Fig. 4. The levels of the fully substituted deutero-ammonia have been determined, and we observe that two vibrational levels one above (2400), and one below (1150), the energy of the mercury transition, are about equally probable transitions for the deutero-ammonia to undergo, but the new lower levels in all the substituted ammonias are progressively moving further away from the mercury energy as deuterium is substituted. It is not until completely substituted ammonia is reached that the higher vibrational level has moved down sufficiently to compete with the lower level as the energy change responsible in the quenching process.

If we place the quenching cross sections measured for the ammonias at their corresponding energy levels on the resonance curve

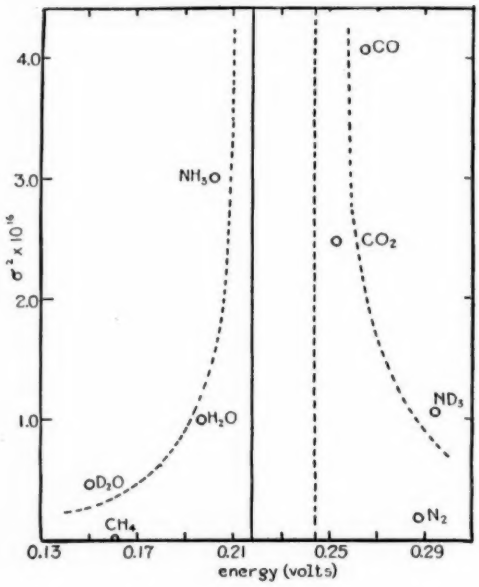

FIG. 5.

as determined by the values of Zemansky and Bates, we notice that if in the case of deutero-ammonia the lower vibrational level (1150) was responsible for quenching, we should expect a very much lower quenching cross section (approximately zero) than that actually measured (1.09×10^{-16}). If, however, the higher level (2400) is responsible for the quenching, we should expect, since the resonance curve is asymmetric, and since the molecules possess $\frac{1}{2}kT$ as kinetic energy, a higher quenching cross section, in spite of the fact that the two levels, both upper and lower, are approximately equidistant from 0.218 volt. Placing the quenching cross section of ND_3 at this higher level fits in with the general form of the curve obtained from a variety of molecules (Fig. 5).

It is of interest to speculate on the probable quenching efficiencies of the mixed ammonias. Although the upper member of the original second vibrational level will probably only move slightly away from the value of 0.218, it is probable that the quenching cross section of these compounds will lie nearer that of deutero-ammonia than that of ammonia, since the statistical weight of this level has been reduced in these non-degenerate cases to a value of 2

from one of 4. It is difficult also to assess the importance of the overtones of the first fundamental frequency. These may in certain cases lie very close to the energy of the $^3P_1 \rightarrow {}^3P_0$ mercury transition, but since the relative probabilities of transition to an overtone level as compared with that to a fundamental are unknown, and since their statistical weight is only 1 as compared with 4, it may be that these factors may counterbalance the effect of closer resonance.

Similar considerations will apply in the case of water vapor. Fig. 4 (b) shows the three fundamental frequencies in the case of water in which the hydrogens have been successively replaced. In this case it is the lower vibrational level which is always responsible for the quenching process, the upper level never being depressed sufficiently to become effective. Reference to Fig. 5 will show that the quenching cross section of D_2O lies very well on the resonance curve at its appropriate energy level. Fig. 4 (c) and (d) show diagrammatically the modes of vibration of ammonia and water corresponding to the different energy levels, and since in the case of ordinary and heavy water the quenching process is concerned with the same frequency of the water molecule, the vibrations of this molecule after quenching will be of the same kind in both cases. Not so, however, in the case of the ammonias where deutero-ammonia after quenching is vibrating in a different way from ordinary ammonia under the same conditions.

An examination of the possible energy changes involved in transitions between vibrational levels other than from the ground state reveals, that some of these changes lie very close to 0.218 volt, and it would be of interest, therefore, in this connection to study the quenching efficiency of such molecules at higher temperatures when a larger number of molecules would be in vibrational levels other than the ground level, and when transitions involving closer resonance would be increasingly possible.

It is impossible to decide from such experiments as these whether the quenching process in the case of ammonia is one involving a change to the metastable state of the mercury or whether the whole of the 4.86 volts of the excitation energy of mercury is taken up by the ammonia molecule. That some such process involving more energy than 0.218 volt is involved is shown by the photosensitized decomposition of ammonia. There is a singlet excited state of ammonia known at a level 5.75 volts above the ground level but because of the large difference in energy, and also because conservation of total spin momentum would not be obeyed, this may be a very improbable process. There may, however, be a triplet state of ammonia between the ground state of ammonia and the excited singlet state, which may be responsible for quenching excited mercury to the ground state. The differences observed in the quenching efficiencies of ammonia and deutero-ammonia would then have to be attributed to the differences in excitation energy of the two molecules due to the differences in zero point energy in the ground and triplet states, and since the position of the triplet state is imperfectly known, it is impossible to assess the energy which would be required in the two cases.

The author is extremely grateful to Professor Hugh S. Taylor for the facilities afforded in these laboratories and also for the helpful interest which he has taken in this work, and to Dr. W. S. Benedict for many helpful discussions and for placing at the author's disposal the results of his spectroscopic analysis of the deutero-ammonias.

Deuterium as an Indicator of Mechanism in the Photo-Decomposition of Ammonia

HUGH S. TAYLOR AND JOSEPH C. JUNGERS,[1] *Frick Chemical Laboratory, Princeton University*

By studying the photolysis of ammonia-deuterium mixtures it has been experimentally demonstrated that the reaction $NH_2+H=NH_3$ is an important feature of the overall photo-decomposition and provides one reason for the low quantum yield observed in the photo-process. It has further been shown that the interaction of hydrogen atoms with ammonia molecules is a process of low efficiency at room temperatures.

IN all recent studies[2] of the photolysis of ammonia in ultraviolet light it has been assumed that the initial process on absorption of light is

$$NH_3+h\nu=NH_2+H$$

and that this is followed, among other processes which lead to nitrogen and hydrogen, by a back reaction $NH_2+H=NH_3$ which may or may not be a three-body process. This reverse reaction is used to account for the low quantum yield (0.25 or less at room temperatures) of a predissociation process which might have been expected to give a quantum yield of unity. Melville[2b] obtained strong evidence in support of this view by showing that the ammonia decomposition was markedly suppressed when atomic hydrogen, produced by means of excited mercury atoms, was simultaneously present in the reaction system.

By making use of deuterium in place of hydrogen in the experiment of Melville we have decisively demonstrated the marked existence of the reverse reaction. In a previous communication[3] on the deutero-ammonias we have shown that they are readily distinguishable from ammonia by means of their ultraviolet absorption spectra, and that semi-quantitative estimates of their respective concentrations can be deduced from such spectra. Accordingly, we have illuminated in a quartz reaction vessel suitable for the spectroscopic measurements,[3] a mixture of 160 mm of ordinary ammonia and 600 mm of pure deuterium gas in the presence of a little mercury. As source of illumination we employed the Hanovia Sc-2537 quartz mercury vapor rare gas discharge tube already described.[3] Of this light source we know that there is light emitted of wave-length around 2100A, adequate to effect photochemical decomposition of ammonia. It is also a rich source of resonance radiation, $\lambda=2536.7$A.

The gas pressures were so chosen as to give satisfactory absorption spectra of the ammonias and to ensure, due to the high concentration of deuterium, that the decomposition of ammonia would not be very rapid. From time to time, after intervals of illumination, the absorption spectra of the mixture were photographically recorded. There was revealed a progressive change in the absorption spectra from that of pure NH_3 to that of an equilibrium mixture of NH_2D, NHD_2 and ND_3. After 48 hours illumination we estimate that the ammonia present contained 70 percent of the hydrogen as the deuterium isotope.

The possibility that these deutero-ammonias arose from interaction of atomic deuterium with molecular ammonia was tested by a second experiment in which the short wave-length light, instrumental in dissociating the ammonia, was reduced by surrounding the light source with a filter of 25 percent acetic acid solution 1.5 cm in thickness. The light source was so disposed as to give a somewhat larger intensity of resonance radiation than in the first experiment. Under these conditions we found a very much reduced production of the deutero-ammonias, about 10 percent of the deuterium compounds being formed in 72 hours illumination. It is not possible

[1] C.R.B. Fellow in Princeton from Louvain University, 1933–34.

[2] (a) Wiig and Kistiakowsky, J. Am. Chem. Soc. **54**, 1806 (1932); (b) Melville, Trans. Faraday Soc. **28**, 885 (1932); (c) Ogg, Leighton and Bergstrom, J. Am. Chem. Soc. **56**, 318 (1934).

[3] Jungers and Taylor, J. Chem. Phys. **2**, 373 (1934).

to say whether even this change did not arise from photo-decomposition of the ammonia and the reverse reaction since the action of the light-filter is possibly not completely efficient and also the photosensitized decomposition of ammonia by excited mercury must have occurred to some extent even in the presence of such an excess of deuterium. The experiment, however, is decisive to this extent, that it indicates that any reactions such as $NH_3+D=NH_2D+H$ or $NH_3+D=NH_2+HD$, followed by a reverse reaction, $NH_2+D=NH_2D$, are processes of low probability in comparison with the reverse process following photo-decomposition. This conclusion is a direct experimental check of the early observation of Bonhoeffer[4] that atomic hydrogen, produced in a Wood's discharge tube, did not interact with ammonia molecules.

Note added June 5, 1934. This last experiment is of importance also in view of the paper by L. Farkas and Harteck,[5] just issued, on the mechanism of photo-decomposition of ammonia as revealed by studies of the stationary hydrogen atom concentration in illuminated ammonia-hydrogen systems. They measured the atom concentration by its influence on the para-hydrogen conversion and are led to the postulate of an equilibrium between hydrogen atoms and ammonia and an intermediate product, NH_4. They assume a kinetic equilibrium

$$NH_3+H \rightleftharpoons NH_4,$$

which is practically on the NH_4 side at room temperatures and on the NH_3+H side at 300°C. They assume a binding energy of 10 kilocals. Our experiment with resonance radiation and deuterium indicates that the NH_4 cannot be a complex in which each of the four hydrogen atoms are equivalent, since if this were so the kinetic equilibrium should yield concentrations of deutero-ammonias equally as well as decomposition of ammonia. Our experiment indicates that the complex, if it exists, is rather of the nature NH_3-D, with the atom bound by the polarization forces of the ammonia molecule and that it decomposes into NH_3 and D. Whether under these circumstances the Farkas-Harteck mechanism is anything other than a three-body recombination of H and NH_2 with NH_3 as the third body, coupled with an alternative decomposition process

$$H+NH_2+NH_3=NH_3+NH+N_2,$$

the ratio of which recombinations and decompositions are 3 : 1, to give the observed quantum yield of 0.25, is indeed problematical. The difficulties which attend their proposal when it is applied to the definite results of Melville on the suppression of photolysis by increased concentration of hydrogen atoms, are inherent also in this latter interpretation. It is doubtful, therefore, whether their proposals, even in the modified form suggested by our experiment, are superior to those mentioned in our introductory paragraph.

We are indebted to Dr. W. S. Benedict for his assistance in interpreting the spectrographic measurements.

[4] Boehm and Bonhoeffer, Zeits. f. physik. Chemie **119**, 385, 474 (1926).

[5] Farkas and Harteck, Zeits. f. physik. Chemie **B25**, 257 (1934).

The Vapor Pressures and Derived Thermal Properties of Hydrogen and Deuterium[1, 2, 3]

R. B. Scott, F. G. Brickwedde, Harold C. Urey and M. H. Wahl, *National Bureau of Standards and Columbia University*

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(1) The vapor pressure equations of liquid and solid, normal deuterium were determined by comparison of the vapor pressure of deuterium with that of liquid, normal hydrogen between 13.9° and 20.40°K. The triple and boiling points of deuterium were found to be 18.58° and 23.5°K, respectively. (2) The changes with time in the vapor pressures of liquid hydrogen and liquid deuterium at 20.4°K, resulting from ortho-para conversions, were investigated. The rate of change of the vapor pressure of liquid deuterium resulting from its natural, self-conversion was found to be less than 1/40th of the natural rate of conversion for liquid hydrogen. (3) From the vapor pressure equations of deuterium and an equation of state, its latent heats were deduced by the use of the Clausius-Clapeyron equation. Two equations of state for deuterium were used: (a) the empirically determined equation for hydrogen, and (b) an equation deduced from an equation of state of hydrogen of a form required by the Bose-Einstein statistics by including the effect of mass in such an equation. The first of these is believed to be the better approximation though the latter might be used with little change in results. The vapor pressure equation required by the third law of thermodynamics has been derived and by the use of the Debye theory values of the zero point energies and Debye Θ's are secured. These Θ's which are used to calculate the heat capacities of solid and liquid deuterium at constant pressure are calculated from the vapor pressure data. The difference between C_p and C_v is much greater for solid hydrogen than for solid deuterium indicating a larger coefficient of expansion in the case of hydrogen. This is to be expected because of the larger zero point energy of hydrogen. The heat capacity under saturation pressure of liquid deuterium is considerably less than that of hydrogen. A recalculation of the distillation data of Urey, Brickwedde and Murphy on the natural mixture of H_2 and HD shows that they secured approximately the enrichment to be expected from the theory and experimental conditions.

SINCE it was by the fractional distillation of liquid hydrogen that we first concentrated deuterium,[3] we were naturally interested in determining the difference in the vapor pressures of the hydrogens responsible for the partial separation effected. Although in the initial stages of the separation one is concerned with the molecules HD and H_2, the investigation reported here has to do with the molecules D_2 and H_2. The difference between the vapor pressures of these isotopic molecules was found experimentally to be much larger than we had calculated[3] upon the basis of accepted theories of the vapor pressures of crystals. At the triple point of ordinary hydrogen (13.92°K), the calculated ratio of the vapor pressure of H_2 to that of D_2 at the same temperature is 3.35, whereas now it is found experimentally to be 10.8. The zero point energies were deduced, however, from the heat capacity of hydrogen under the saturation pressure instead of from the heat capacity at constant volume, data on which are not available. It appears that the difference between our previously calculated ratio of vapor pressures and that found here is due to larger zero point energies than those previously calculated. It appears further that the difference, $C_p - C_v$, is smaller for deuterium than for hydrogen, a situation which seems reasonable in view of the very large difference in the zero point energies of the solids, as will be shown later.

The deuterium used in this experiment was prepared by the electrolysis of a sample of heavy water of high concentration. Calculations using the usual fractionation factors for such an electrolytic process showed that it should be approximately 99.9 percent deuterium. It is, of course, difficult to be certain that a small

[1] Published with the approval of the Director of the National Bureau of Standards.

[2] The results contained in this paper were reported at the February and April, 1934 meetings of the American Physical Society in New York and Washington, respectively (Phys. Rev. **45**, 565 and 762 (1934)), and at the symposium on deuterium during the meeting of the American Chemical Society in St. Petersburg, March, 1934. The more theoretical aspects of the problem were presented by one of us as the Willard Gibbs Medal Award address in Chicago, April 28, 1934.

[3] Urey, Brickwedde and Murphy: *A Hydrogen Isotope of Mass 2 and Its Concentration*, Phys. Rev. **40**, 1 (1932).

hydrogen impurity did not get into this sample. However, this sample of deuterium has the lowest vapor pressure of any we have investigated.

Description of the Apparatus

Fig. 1 represents diagrammatically the apparatus used in making the vapor pressure measurements. The glass flask F which contained the sample of deuterium was connected with a capsule-shaped glass bulb, at the end of a

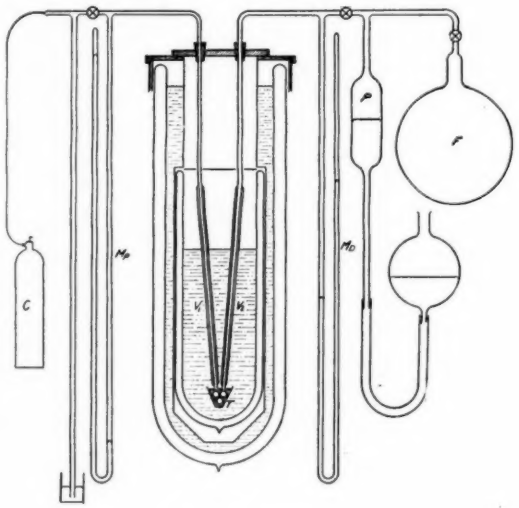

Fig. 1. The cryostat.

vacuum jacketed tube V_2, in the inner Dewar flask of a liquid hydrogen cryostat. The vapor pressure of the solid or liquid deuterium condensed in the capsule, when this inner Dewar flask was filled with liquid hydrogen, was measured on an oil (n-butyl phthalate) lubricated mercury manometer, M_D. By means of a hand operated mercury pump P, the deuterium sample was pumped from the flask F and afterwards returned to it.

Normal hydrogen, from a small cylinder C, was condensed in a glass capsule at the end of the tube V_1, and its vapor pressure was measured on the manometer M_P. The hydrogen as it flowed from the cylinder contained air as an impurity, the molecular concentration of which was not greater than 0.02 percent. Since the effect of solid oxygen on the vapor pressure of the liquid hydrogen had not been investigated, the hydrogen as it flowed from the cylinder was passed over hot copper at 600°C, and then through a liquid air trap.

Temperatures were determined with a four lead, pure platinum, resistance thermometer, T, whose resistance at 0°C was 28.8 ohms. The platinum coil, wound on a mica cross,[4] was sealed in a platinum case filled with helium, the four leads, current and potential, being brought out through a soft glass seal. The outside diameter of the platinum case was 0.5 cm and the overall length of the thermometer 5 cm. It was calibrated by comparison with the vapor pressure of freshly condensed normal hydrogen, using the vapor pressure equation discussed later for the determination of temperatures.

The temperature of the liquid hydrogen bath in the inner Dewar vessel was varied by means of a large capacity vacuum pump and a series of hand operated valves interposed between the pump and the vacuum connection at the top of the cryostat. With the aid of a fine adjustment valve and an oil filled manometer, especially designed for the purpose, it was possible to hold the pressure in the vapor space over the liquid hydrogen bath constant to within ± 0.2 mm of mercury.

Since the liquid hydrogen bath was not stirred, special precautions were taken to insure that the thermometer, and the hydrogen and deuterium condensates whose vapor pressures were to be investigated, were all at the same temperature. The manometer tubes, leading down to the capsules through the liquid hydrogen bath, were vacuum-jacketed, and the thermometer and two glass capsules were cast in a low melting point alloy metal block, as indicated in Fig. (1).

Experimental and Calculated Results

Vapor pressure of deuterium

In Table I are recorded a series of determinations of the vapor pressures of normal hydrogen and deuterium. The observed vapor pressures are given in columns 3 and 5. Column 4 is obtained from column 3 by correcting for the change with time of the vapor pressure of the

[4] For the method of winding these coils, see C. H. Meyers, Bur. Standards J. Research 9, 807 (1932).

TABLE I.

1 Age of condensed states hrs.	2 Temperature °K	3 Observed vapor pressure of hydrogen mm of Hg	4 Vapor pressure of normal hydrogen (calculated) mm of Hg	5 Vapor pressure of normal deuterium (observed) mm of Hg
0	20.334	749.8	749.8	252.0
0.5	19.969	672.0	672.0	218.5
1.2	19.330	550.3	550.0	168.5
1.5	19.167	522.0	521.7	157.1
2.4	18.953	486.5	486.0	143.2
2.8	18.945	485.3	484.9	142.4
3.0	18.182	372.8	372.4	97.7
3.6	17.479	287.3	287.0	65.5
4.0	16.463	190.6	190.3	35.0
4.5	15.188	106.2	106.1	14.2

hydrogen resulting from the conversion of ortho- to para-hydrogen. The ages of the condensed state at the time of the observations are recorded in column 1. The results of an investigation of the change of the vapor pressures of hydrogen and deuterium with time are presented below. The temperatures were calculated from the vapor pressures of normal hydrogen recorded in column 4, with the equation,

$$\log_{10} P(\text{mm of Hg}) = 4.6633 - 44.7291/T + 0.02023T. \quad (1)$$

This was deduced as the best fit for the experimental data on (1) the vapor pressure of liquid hydrogen, (2) the latent heat of vaporization, and (3) deviations of the molecular volume of the vapor from the ideal gas. All published vapor pressure measurements were considered, but this equation agrees best with the latest Leiden determinations.[5]

We have tried the use of two equations of state in our calculations. The following equation was deduced from the latest experimental determinations of the virial coefficients[5a] for hydrogen:

$$PV = RT(1 - 0.0381/V(1 + 1150/T^2)), \quad (2)$$

where the volume is measured in liters. The latent heat at the boiling point calculated from these equations agrees exactly with Simon and Lange's[6] experimental value and differs by only 0.3 percent at the triple point.

[5] Keesom, Bijl and van der Horst, Proc. Amst. Acad. **34**$_2$, 1223 (1931).

[5a] van Agt and Onnes, Leiden Comm. No. 176b (1925).

[6] Simon and Lange, Zeits. f. Physik **15**, 312 (1923), see footnote 8.

It may be expected that deuterium will not have exactly the same equation of state as hydrogen. If the entire imperfection of these gases could be accounted for by the Bose-Einstein gas theory, the equation of state should be of the form,

$$PV = RTf(V^{\frac{1}{3}}T).$$

The equation,

$$PV = RT(1 - 13.192/VT^{\frac{1}{3}}) \quad (3)$$

agrees with the experimental data on hydrogen about as well as Eq. (2), though the value of the constant is much larger than that required by the theory for an ideal gas. The correction terms in the Bose-Einstein theory contain the mass to the same power as the temperature, and hence the maximum difference to be expected in the equations of state of hydrogen and deuterium can be estimated. The equation of state of deuterium would then be

$$PV = RT(1 - 4.6707/VT^{\frac{1}{3}}). \quad (4)$$

This equation of state for deuterium makes the maximum correction possible for the difference between the equations of state for hydrogen and deuterium, though it seems probable that the equation of state of deuterium will be more nearly the same as hydrogen. The use of either of the equations of state (2) or (4) for deuterium makes but little difference in the derived data, but Eq. (2) does fit the experimental and calculated results better than Eq. (4) does.

Fig. 2 is a graph of the logarithm of the vapor pressure of normal hydrogen against that of deuterium (columns 4 and 5 of Table I). The lines fitting the lower and upper ranges of pressures are the vapor pressure curves of solid and liquid D_2, respectively; their point of intersection (18.5_8°K) is the triple point of D_2. It is interesting to note that the observations plotted as in Fig. 2 fall along straight lines to within the precision of the results, whereas there is noticeable curvature of the graphs of the logarithms of the vapor pressures plotted against $1/T$.

The experimental data can be represented by the empirical equations,

$$\log_{10} P(D_2 \text{ liquid}) = -1.363 + 1.310 \log P(H_2 \text{ liquid}), \quad (5)$$

$$\log_{10} P(D_2 \text{ solid}) = -1.954 + 1.534 \log P(H_2 \text{ liquid}). \quad (6)$$

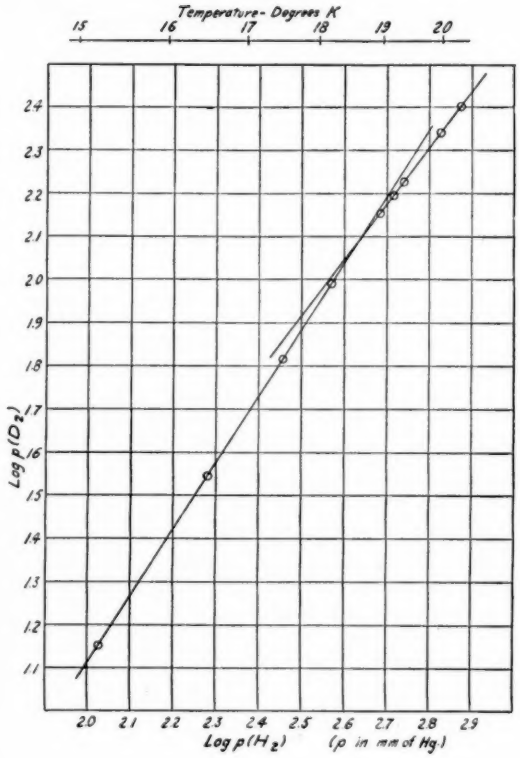

FIG. 2.

With Eq. (1), these become

$$\log_{10} P(\mathrm{D_2\ liquid}) = 4.7459 - 58.5951/T + 0.02650T, \quad (7)$$

$$\log_{10} P(\mathrm{D_2\ solid}) = 5.1995 - 68.6144/T + 0.03103T. \quad (8)$$

Since the vapor pressures of hydrogen and deuterium were compared directly, Eqs. (5) and (6) are independent of the temperature scale, whereas Eqs. (7) and (8) are not.

In Table II are listed the vapor pressures of normal hydrogen and deuterium at their boiling points, and triple points, calculated from these equations.

Although the values given by these equations and in Table II are accurate for the sample investigated, they may be subject to revision when purer deuterium is secured. As stated above, there are reasons for believing that the deuterium used here was of very high purity. The results reported here are not in good agreement with those of Lewis and Hanson,[7] who

[7] G. N. Lewis and W. T. Hanson, Jr., J. Am. Chem. Soc. **56**, 1001 (1934).

TABLE II.

	Vapor pressure in mm of Hg	
	H_2	D_2
23.5°K (Boiling point of normal D_2)	1740	760
20.38 (Boiling point of normal H_2)	760	257
18.58 (Triple point of normal D_2)	429	121
13.92 (Triple point of normal H_2)	54	5

compared the vapor pressure of a supposedly "pure" sample of deuterium with that of para-hydrogen. For the same temperatures the vapor pressure values of Table II are lower than those of Lewis and Hanson, indicating that the sample of deuterium used for the investigations reported here was purer than theirs by about 0.5 percent. It is possible that the conversion of their reference sample of hydrogen to para-hydrogen was not as complete as they supposed, the error resulting, thereby, being in the direction to make their values for the vapor pressure of deuterium too high.

Latent heats of deuterium

Table III is a table of latent heats of hydrogen and deuterium. The values for hydrogen are the results of calorimetric determinations,[8] those for deuterium were obtained by calculation from the slopes of the vapor pressure curves using the Clausius-Clapeyron equation. In the absence of experimental data, it was assumed that the molecular volumes of the liquid and solid deuterium between 13.92° and 20.38° are equal to those of liquid hydrogen at the same temperature.* The volumes of liquid hydrogen were taken from the *International Critical Tables*, Vol. I. Under ΔH(ideal) are given the heats of vaporization to a gas at zero pressure, using

[8] Simon and Lange, Zeits. f. Physik **15**, 312 (1923). The equation of Simon and Lange was modified to allow for the difference in the temperature scales. This modified equation yields the same latent heats at the same thermal states as does the original equation, $Lv = 219.7 - 0.27(T - 16.63)^2$.

* Keesom and Lisman, Proc. Roy. Acad. Amst. **35**, 607 (1932) have given the fusion curve of hydrogen. From these values it is possible to deduce with the aid of the equation

$$dP/dT = \Delta H_f/T\Delta V$$

the values of ΔV, and assuming that the molecular volume

TABLE III.

	H_2		D_2		
T	ΔH	ΔH Ideal	*ΔH	*ΔH Ideal	†ΔH Ideal
13.92	245.7 (28.0)	247.7 (28.0)‡			
13.92	217.7	219.7	340.8	340.9	341.1
15.188			345.4	345.7	345.8
16.43			349.6	350.2	350.0
17.479			352.7	353.7	353.7
18.182			354.5	355.9	355.9
18.58	218.7	224.8	355.4 (52.3)	357.1 (52.3)	357.2 (52.4)‡
18.58			303.1	304.8	
18.945			304.0	305.9	
18.953			304.0	305.9	
19.167			304.4	306.5	
19.330			304.8	306.9	
19.969			306.0	308.6	
20.334			306.6	309.6	
20.38	215.9	225.3			

* The values given in these columns were calculated from the empirical vapor pressure equation.

† The values given here were calculated from the equation, $\Delta H=\Delta H_0+(5/2)RT-H_s$, from values given in a following paragraph, where H_s is taken as a Debye energy with $\Theta_2'=100$.

‡ The quantities in parentheses are the latent heats of fusion per mole. At the triple points latent heats of vaporization and sublimation are given.

Eq. (2) for both gases. The heat content of the gas is then given by the equation,

$$H=H_0+(5/2)RT-(RT/V)0.0381(1+3450/T^2), \quad (9)$$

and it is only necessary to add the values of the last term to the values in column 4 to secure those in column 5 of Table III. If Eq. (4) is used for diplogen, the value of ΔH(ideal) for deuterium at 20.334° is decreased by 4.15 cals., and other values in the table are decreased by small amounts. The heat of fusion is changed from 52.3 cals. to 53.1 cals.

of liquid hydrogen as given in the literature is correct, the molecular volume and density of solid hydrogen at the triple point can easily be calculated. When calculated in this way, the density is found to be larger than any values recorded. This would indicate that the values for the density of solid hydrogen are very inaccurately known. The correction for the volume of the solid is small in any case, amounting to only 1.8 cals. as a maximum. The error introduced by using the volumes of liquid protium is only about 10 percent of this, or about 0.2 cal. For this reason, we have not attempted to estimate the volume of solid deuterium any more accurately.

On the change of the vapor pressure of deuterium with time

Figs. 3 and 5 are graphs of determinations of the vapor pressures (reduced to 20.38°K) of liquid hydrogen and liquid deuterium plotted against the age of the liquid state.

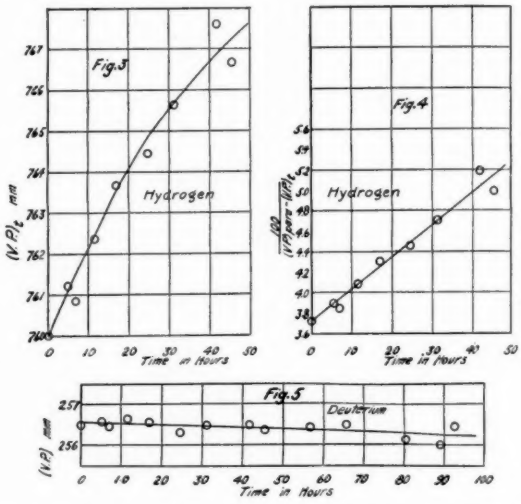

FIG. 3. The change of vapor pressure of hydrogen with time.
FIG. 4. The ortho-para conversion of hydrogen.
FIG. 5. The para-ortho conversion of deuterium.

Fig. 4 is a plot of one hundred times the reciprocal of the difference between the vapor pressure of para-hydrogen and the vapor pressure of the liquid hydrogen, originally normal, the age of whose condensed state is the abscissa. That the observations plotted in Fig. 4 fall along a straight line is a consequence of the conversion of ortho- to para-hydrogen in the liquid phase being a bimolecular change.[9] For such a change, the rate of decrease of the ortho-hydrogen concentration ($-dx/dt$) is proportional to the square of the concentration,

$$-dx/dt=kx^2. \quad (10)$$

The slope of the line is $k/[(\text{v.p.})_{\text{para}}-(\text{v.p.})_{\text{ortho}}]$. The velocity constant k of the conversion change in the liquid phase was calculated using 786.86 mm of Hg for the vapor pressure of para-hydrogen and 751.00 mm for ortho-hydrogen at the temperature at which the vapor pressure of

[9] Cremer and Polanyi, Zeits. f. physik. Chemie **B21**, 459 (1933).

freshly condensed normal hydrogen is 760.00 mm (20.38°K).[10] The value obtained for k was 0.0114 per hour when concentrations are expressed in terms of mol fractions. This is in agreement with the value obtained by Cremer and Polanyi[9] using the thermal conductivity method of analysis to follow the change in concentration of ortho-hydrogen. Their values range from 0.010 to 0.013, averaging 0.0118. The agreement is better than the accuracy of the work reported here and that of Cremer and Polanyi as well.

It is interesting to note that a small amount of solid oxygen in the liquid hydrogen markedly increased the rate of conversion, as was made manifest by a proportionately greater rate of increase of vapor pressure. The rate of increase for a sample containing about 0.01 percent O_2 was greater by a factor of 3 than the rate after the oxygen had been removed by passing the hydrogen over copper at 600°C.

Referring to Fig. 5, the straight line which is the best fit for the observations, reduced to 20.38°K, of the vapor pressure of originally normal deuterium plotted as a function of the age of the condensed state indicates a decrease of the vapor pressure of deuterium with time. However, F. G. Brickwedde, R. B. Scott and H. S. Taylor[11] have measured the vapor pressure of deuterium passed over a conversion catalyst at liquid hydrogen temperatures and find that at 20.38°K the vapor pressure of the "converted" deuterium is about 5 mm of Hg greater than the vapor pressure of normal deuterium. It was concluded that the uncatalyzed change of the vapor pressure of liquid normal deuterium with time is too small for measurement with the apparatus used in this investigation. The observations reported here show that the rate of change of the vapor pressure of normal deuterium with time is less than 1/40th of the rate of change of the vapor pressure of normal hydrogen.

[10] Considering all the published determinations of the vapor pressure of para-hydrogen at the boiling point of normal hydrogen, 786.86 mm of Hg was selected as the most probable value for the vapor pressure of para-hydrogen. The vapor pressure of ortho-hydrogen (751.00 mm) was calculated from the vapor pressures of para- and normal hydrogen.

[11] F. G. Brickwedde, R. B. Scott and H. S. Taylor, *The Vapor Pressure of Ortho- and Para-Deuterium* to be published in this Journal.

Calculation of the Vapor Pressure Equation with the Third Law and the Debye Theory of the Solid State

Simon and Lange found that the heat capacity of solid hydrogen under saturation pressure could be described by the use of a Debye function using a Θ_1' of 91. It is assumed here that it is also possible to describe the heat capacity of solid deuterium at zero pressure in a similar way. The Θ's which are used for the thermodynamic functions at constant pressure will be indicated by primes. The subscripts 1 and 2 will be used to designate the values of the quantities for hydrogen and deuterium, respectively.

In the paper by Urey, Brickwedde and Murphy,[3] an approximate theory for the ratio of vapor pressures of solid H_2 and solid D_2 was developed, assuming (1) that the vapor pressure could be calculated using the third law of thermodynamics, (2) that the zero point energies were given by the Debye theory of the solid state, namely $(9/8)R\Theta$, and moreover, (3) that the Θ's for the two hydrogens varied inversely as the square roots of the molecular weights. The ratio of vapor pressures calculated for molecules of masses 2 and 4 was 3.354 at the triple point of hydrogen, which is in marked disagreement with the experimental results reported in this paper. For hydrogen the value of Θ_1' derived by Simon and Lange[6] from the heat capacity under the saturation pressure was used. This cannot give the correct Θ_1 for it would be necessary to derive this from the heat capacity at constant volume, and since the heat capacity at constant volume must be less than the heat capacity at constant or saturation pressure, the true Θ_1 must be greater than the value used, namely 91. With values for the coefficients of expansion and of compressibility of hydrogen from the *International Critical Tables*, the difference $C_p - C_v$ is calculated to be about 37 cals., where in fact the heat capacity of hydrogen under saturation pressure is about 1.2 cals. It is obvious that these coefficients of expansion and compressibility are very inaccurately known. Moreover, the assumption that the internal rotational and vibrational energies in the solid and gaseous states are the same will be discussed later. Also, it was assumed that the gases

followed the ideal gas laws. This, of course, is only approximately true, but the corrections necessitated by this approximation are small.

The free energy of the gaseous hydrogen at a pressure P can be set equal to the free energy at a very low pressure P^* approaching zero $+\int_{P^*}^{P} V dP$. The free energy of the gas at pressure P^* is given accurately by the Sackur-Tetrode equation,

$$F = H_0 + (5/2)RT - RT(\ln M^{3/2}T^{5/2}P^{*-1}) + CT. \quad (11)$$

The free energy of the solid is equal to its free energy under pressure $P^* + \int_{P^*}^{P} V_s dP$, and if the volume of the solid can be regarded as constant with changing pressure, this additional term is equal to $V_s P$. At equilibrium these free energies must be equal. Equating them and introducing the equation of state (2), we secure for the vapor pressure equation,

$$\ln P = -\frac{\Delta H_0}{RT} + \frac{5}{2}\ln T + \frac{3}{2}\ln M + 2.30259i + \frac{V_s P}{RT} + \frac{F_s}{RT} + \ln\left(1 - \frac{0.0381}{V}\left(1 + \frac{1150}{T^2}\right) + \frac{2\times 0.0381}{V}\left(1 + \frac{1150}{T^2}\right)\right), \quad (12)$$

where ΔH_0 is the heat of vaporization at absolute zero, i is the chemical constant equal to -1.5882 according to Birge,[12] and F_s is the free energy of the solid at zero pressure. The correction term due to the imperfection of the gas has been calculated by calculating the volume from the equation of state at the pressures given by the empirical vapor pressure Eq. (8). As before, we have taken the volume of the solid deuterium as equal to the volume of liquid hydrogen as given by the *International Critical Tables*. These correction terms for deuterium are small.

As stated above, it is assumed that F_s can be described by the use of a Debye Θ_2'. By trial and error it is found that constant values for ΔH_0 can be secured if Θ_2' is taken as equal to 100.[13]

The values of ΔH_0 calculated in this way for the four temperatures for which measurements have been made give the values in Table IV.

TABLE IV.

T	15.188	16.463	17.479	18.182	
ΔH_0	276.11	275.97	276.09	276.08	Av. 276.06

The average value of ΔH_0 determined in this way is 276.0 cals./gram mole. By using equation of state (4) and by making a similar calculation, ΔH_0 equals 276.2 cals./gram mole and $\Theta_2' = 105$. Thus it seems to be impossible to change the value of ΔH_0 except by small amounts and that Θ_2' is correct within about ± 5 units.

This Θ_2' is one which will describe the thermodynamic functions for solid deuterium in this range of temperature at zero pressure, though with the small vapor pressures involved, no observable difference can be expected if the thermodynamic functions are those under the saturation pressures. The heats of vaporization recorded in the last column of Table III for solid deuterium have been calculated using the constants derived here. The agreement between the heats of vaporization calculated from the empirical equation (column 5) and the equation given in this section is very good and indicates that Eqs. (12) and (8) give the vapor pressures equally well.

Simon and Lange[6] have determined the heat of vaporization and the heat of fusion of the solid hydrogen. They found that the heat of sublimation of solid hydrogen at the triple point is 245.8 cals./mole. This is equal to the heat content of the vapor at a pressure of 5.38 cm mercury minus the heat content of solid deuterium at the triple point. With our equation of state and Eq. (9),

$$\Delta H = \Delta H_0 + (5/2)RT - (RT/V)0.0381(1 + 3450/T^2) - H_s \quad (\Theta = 91).$$

Substituting the numerical values, we find that $\Delta H_0 = 182.9$ instead of 183.4 as given by Simon.

CALCULATION OF THE ZERO POINT ENERGIES

If it is assumed as it was by Urey, Brickwedde and Murphy that the heat of vaporization of the vibrationless solid to the motionless gas at

[12] Birge, Rev. Mod. Phys. **1**, 65 (1929).

[13] The values of F_s as a function of Θ_2' are given in the Handbuch d. Physik, Volume 10, page 369.

absolute zero, represented by χ, is the same for hydrogen and deuterium, and that the ratio of the zero point energies of the two solids is inversely proportional to the square root of the molecular weights, it is possible to calculate the value of χ and of the zero point energies. Thus

$$\chi = E_0(H_2) + 182.9 = E_0(D_2) + 276.0$$

and

$$E_0(H_2)/E_0(D_2) = (4.0273/2.0156)^{\frac{1}{2}}.$$

From these equations, $\chi = 501.2$, $E_0(H_2) = 318.3$ and $E_0(D_2) = 225.2$. The corresponding Θ's are given by the equation $\Theta = 8/9E_0/R$, and thus we find that $\Theta_1 = 142.4$ and $\Theta_2 = 100.7$. These should be used to calculate the heat capacity and other thermodynamic properties at constant volume. The Θ_1 is greater than the Θ_1' and hence the heat capacity of hydrogen at constant pressure is greater than that at constant volume. The difference between Θ_2 and Θ_2' is so small that we cannot be certain that this is not altogether due to the nature of the calculation, and thus we may say that these quantities would indicate that the heat capacity at constant pressure and at constant volume for deuterium are equal. With the well-known thermodynamic relation $C_p - C_v = \alpha^2 VT/\beta$, where α and β are the coefficients of thermal expansion and compressibility respectively, it is seen that the coefficient of thermal expansion for deuterium must be very small. This is surprising and leads us to question the assumption upon which this calculation is based.

Effect of Rotational and Vibrational Energy Changes

In the calculations which we have made, it is assumed that there is no change in the rotational and internal vibrational energies of the molecules in going from the solid to the gaseous state. The Raman spectra data on liquid hydrogen show that energy differences of the rotational states are within experimental error (approximately 1 wave number) equal to the differences in the gaseous state, and that the vibrational frequency in the liquid state differs from its value in the gaseous state[14] by about 10 cm^{-1}. This difference is not much greater than the experimental error as nearly as we can judge. It may be expected that the difference may be even larger in the solid state. Recent work by Salant, Sandow and Callahan[15] on the Raman spectra of the hydrogen halides show very appreciable differences in the vibrational frequencies in the gaseous, liquid and solid states, and that the frequencies are uniformly less in the condensed phases. This would affect the heat of vaporization since it would be necessary to supply energy to the internal degrees of freedom in the process of vaporization. If the change in vibrational frequency for hydrogen is 10 cm^{-1} and if the percent change in the vibrational frequencies of deuterium is the same as that for hydrogen, the heats of vaporization would be increased by approximately 14 and 10 cals., respectively, for hydrogen and deuterium. In order to secure the contribution to the heats of vaporization at 0°K due to the potential energies between the molecules the previously calculated ΔH_0's must be decreased by 14 and 10 cals., respectively. If there is such a difference between the internal vibrational energies for the solid and vapor states, these reduced ΔH_0's should be introduced into Eq. (13) for the calculations of the Eo's. The Θ's would be increased, thus making $\Theta_2' = 106.4$ and hence somewhat larger than Θ_2.

Such a correction would still leave the heat capacity at constant pressure for deuterium very nearly equal to its heat capacity at constant volume. However, any such correction would change the values of the Θ_1 and Θ_2 by the same percentage, and thus the heat capacity of deuterium at constant volume will always be larger than that of hydrogen, as is to be expected. This means that the difference between the heat capacities at constant pressure and constant volume will always be less for deuterium than for hydrogen, and hence the ratio of the square of the coefficient of expansion to the coefficient of compressibility will be less for deuterium than for hydrogen. One might expect the coefficient of compressibility of hydrogen to be larger than this coefficient for deuterium, and hence, in order

[14] J. C. McLennan and J. H. McLeod, Roy. Soc. Canada, Trans. **23**, Section 3, 19–20 (1929); McLennan, Smith and Wilhelm, ibid. 279–282 (1929).

[15] Salant and Sandow, Phys. Rev. **37**, 373 (1931). Salant and Callihan, Phys. Rev. **43**, 590 (1933).

to account for the difference in the ratio, it must be assumed that the coefficient of thermal expansion of deuterium is less than that for hydrogen. This conclusion seems reasonable because the zero point energy of hydrogen amounts to about 64 percent of the value of χ, while for deuterium it is only 46 percent of this quantity. As energy is acquired by the vibrating solid, the oscillators become more anharmonic and hence the volume of the solid increases. The high energy oscillators of hydrogen should be more anharmonic in character than the high energy oscillators of deuterium, and hence it is reasonable to expect that hydrogen should expand more rapidly which would be in accordance with our conclusions.

It follows, of course, that the ratio of the zero point lattice energies will not be exactly proportional to the square root of the molecular weights if this anharmonic character is considered, and in fact that the ratio of the zero point energies of hydrogen to that of deuterium will be less than that assumed. The zero point energy of both hydrogen and deuterium are increased over that calculated above, and thus, their Θ's are larger and the heat capacity at constant volume calculated in this way is decreased, again bringing the whole calculation to a more understandable situation.

Pauling[16] has considered the rotational energy of hydrogen molecules in the solid state, for the special case of free rotation or an oscillatory rotation in a plane. He gives reasons for believing that the height of the potential energy hill corresponding to a rotation of the molecule through 180° is about 112 cals./mole. This theory cannot be used for a rotator in space, but the application of the perturbation theory to this problem, if the height of the potential energy hill is small, as compared with the energy difference of the lowest rotational states, can be made by well-known methods. In this way the energies of the lowest rotational states of the perturbed rotator in space are found to be those of the third column of Table V. The potential energy curve is assumed to be of the same form as that used by Pauling, namely, $V=V_0(1-\cos 2\theta)$. If we use Pauling's value for V_0, namely 56, it is immediately evident that there is a very large difference in energy between the 1, 0 and the 1, ± 1 states, and thus, the ortho-hydrogen in the solid phase would be in the lower of these two states. Thus the entropy of hydrogen as determined from the heat capacity curve would not agree with the observed value.[17] This is due to the fact that part of the degeneracy of the first rotational state would have disappeared at these temperatures. Hence, the height of the potential energy hill must be very much smaller than was assumed by Pauling. If V_0 is smaller, say 28 cals./mole, a maximum would occur in the heat capacity in the region of about 10° absolute, which again is not in agreement with experiment. It must be concluded that the value of V_0 is small, something like 15 cals./mole, or less. Taking this value, one secures for the change in energy states in the solid the values given in the last column of Table V.

TABLE V.

J	M	ΔE	ΔE (cals./mole)
0	0	$4/3\ V_0$	20
1	0	$4/5\ V_0$	12
1	± 1	$8/5\ V_0$	24

At the absolute zero, all the molecules in the first rotational state would occupy the level, J, $M=1$, 0. Since ΔH_0 was deduced by extrapolation from higher temperatures where very nearly statistical distribution between the states exists, in proportion to the *a priori* probabilities, and since at higher temperatures the mean energies of the states $J=0$ and $J=1$ do not depend on the temperature, a value for ΔH_0 was obtained which does not depend upon the differences in rotational energy of Table V. Hence, our extrapolation to absolute zero does not include any rotational effect of this kind. Moreover, since it is necessary to assume a very low value of the potential energy hill in solid hydrogen, it follows that the calculated values also hold for deuterium, and hence, that there is practically free rotation in the case of solid deuterium.

Throughout this discussion it is assumed χ to be the same for solid hydrogen and deuterium

[16] L. Pauling, Phys. Rev. **36**, 430 (1930).

[17] Giauque, J. Am. Chem. Soc. **52**, 4816 (1930).

and this assumption may not be correct. Bernal[18] has shown that the molecular volume of solid deuterium oxide is less than that of ice and similarly the molecular volumes of solid hydrogen and deuterium may not be identical. If this were the case, the values of χ and the restoring forces would hardly be the same in the two cases. Hence the ratio of the zero point energies would not be the inverse of the square roots of the molecular weights. Both of these assumptions may need revision later.

We can conclude that the zero point energies and the χ for solid hydrogen and deuterium are greater than those recorded above, and that $C_p - C_v$ is considerably greater for hydrogen than for deuterium and hence that the coefficient of expansion of hydrogen is greater than that of deuterium.

Heat Capacities of Hydrogen and Deuterium

The heat capacities of the solids were calculated using the Θ's and Θ''s derived in the preceding sections assuming as before that they follow the Debye functions. The values thus calculated are listed in Table VI.

The heat capacities of the liquids can be secured from the relation,

$$d\Delta H_{(\text{ideal})}/dT = \Delta C = (5/2)R - C_{s(\text{liquid})}.$$

It is found that C_s is approximately equal to a constant $\times T$ both for hydrogen and deuterium. The heat capacity of liquid hydrogen derived from the vapor pressure equation and the equation of state used here is equal to $0.2314T$. The values calculated in this way are listed in Table VI together with the values calculated from Simon and Lange's empirical equation based on their calorimetric measurements. The agreement between the two sets of values indicates the reliability of heat capacity data calculated from vapor pressure data and the equation of state.

In the same way, the heat capacities of liquid deuterium have been calculated and listed in Table VI. The results indicate that the heat capacity of liquid deuterium is considerably less than that of liquid hydrogen and that there is less difference in the heat capacities of liquid and solid deuterium at its triple point and under its saturation pressure than of liquid and solid hydrogen at its triple point and under its saturation pressure.

Table VI.

	Solid			
	H_2			D_2
T	C_s $\Theta_1' = 91$	C_v $\Theta_1 = 142.4$	$C_{p=0}(C_s)$ $\Theta_2' = 100$	C_v $\Theta_2 = 100.7$
10	0.59	0.16	0.45	0.44
11	0.76	0.21	0.59	0.58
12	0.94	0.28	0.74	0.73
13.92	1.32	0.42	1.07	1.06
16	—	—	1.46	1.43
18	—	—	1.84	1.82
18.58	—	—	1.96	1.92

	Liquid		
	C_s (S. & L.)	C_s (this paper)	C_s
13.92	3.19	3.22	—
16	3.62	3.70	—
18	4.02	4.17	—
18.58	4.15	4.30	2.20
19	4.24	4.40	2.26
19.5	4.34	4.51	2.32
20	4.44	4.63	2.38
20.38	4.53	4.72	2.42

The Vapor Pressure of Solid Hydrogen-Deuterium

Urey, Brickwedde and Murphy gave an approximate calculation of the ratio of vapor pressures of the solid hydrogen and the solid hydrogen-deuterium.* The results of this paper make possible a better estimate of this ratio. If it is assumed that the Θ's are inversely proportional to the square roots of the molecular weights, the calculated Θ_{12} for the hydrogen-deuterium solid equals $\sqrt{\frac{2}{3}}\Theta_1$ and is 125. If further it is assumed that the Θ_{12}' is between the Θ''s of the hydrogen and deuterium, i.e., about 97, the ratio of the vapor pressures of hydrogen and hydrogen-deuterium at 13.92°K should be 2.42. With this in the Rayleigh distillation formula, it is possible to calculate the enrichment which should have been secured

[18] Bernal, Proc. Roy. Soc. **A144**, 24 (1934).

* The ratio of the vapor pressures calculated for these two was given as 2.698. This is unfortunately in error. We neglected the factor 3/2 in the last term of our Eq. (6), Phys. Rev. **40**, 4 (1932). The correct value should have been 2.23.

in the original distillations made by simple evaporation 2 mm of Hg above the triple point pressure. The hydrogen used in these experiments was prepared electrolytically from cells which had been freshly filled with ordinary water. The hydrogen discharged from these cells, as is now known, should contain considerably less deuterium than natural hydrogen. It seems reasonable to assume that the hydrogen used in these experiments contained about 1 part deuterium in 25,000. The ratio of the original volume of liquid hydrogen to the final volume was approximately 4000. Substituting in the Rayleigh equation,[3] it is found that the final sample should have contained approximately 1 part in 200 of deuterium instead of 1 part in 1100 as found by the mass-spectrograph analysis. Or, if the observed fractionation factor is calculated using 1 part in 25,000 for the original concentration, and one part in 1100 for the final concentration, one obtains 2.1 for the ratio of the vapor pressure of hydrogen to that of hydrogen-deuterium at 13.92°K. Because of its low surface tension and density, boiling liquid hydrogen readily forms a spray which is carried along with the vapor in a distillation. It appears, therefore, that the enrichment secured was about what should be expected from the theory.

The Raman Spectrum of Heavy Water Vapor

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The Raman spectrum of heavy water vapor was obtained by using water having a $d^{20}_{20}=1.073$, at two atmospheres pressure. A line $\Delta\nu=2666$ cm^{-1} was found for D_2O and $\Delta\nu=2718$ cm^{-1} for HDO. The other line expected from the work of Wood on liquid heavy water in the region $\Delta\nu=3700$ cm^{-1} was not found. The line $\Delta\nu=3650$ cm^{-1} of H_2O was resolved into a doublet $\Delta\nu=3646.1$ cm^{-1} and $\Delta\nu=3653.9$ cm^{-1}. An attempt has been made to explain the Raman spectrum of H_2O empirically by using the data of Mecke on the infrared absorption spectrum of H_2O.

EXPERIMENTAL

THE apparatus used in the present investigation was essentially the same as that employed by one of us[1] previously in obtaining the Raman spectrum of ordinary water.

In order to utilize a long scattering tube to the best advantage it is necessary to make the distance from the condensing lens to the scattering tube large compared to the distance from the lens to the slit of the spectrograph. Necessarily the fulfillment of this condition produces a very small image, which must be accurately focussed on the slit of the spectrograph. This adjustment can be made quite accurately in the following manner. After the scattering tube has been lined up, the achromatic condensing lens is put in the proper position to focus the image on the slit of the spectrograph. The prisms are then removed from the spectrograph and an auxiliary telescope is aimed down the collimator and the slit brought into sharp focus. The condensing lens is then adjusted until the two tiny arcs of light caused by the light diffracted by the diaphragm in the scattering tube come into sharp focus. The necessity for a critical focus of this small image is best appreciated when one considers the fact that in the present case the actual useful length of the spectral lines on the photographic plate was only 0.25 mm.

From a sample of heavy water $d_{20}^{20}=1.048$ the Raman spectrum of the liquid was obtained. A reproduction of this spectrogram is shown in Fig. 1b. This sample had been purified by a distillation from alkaline $KMnO_4$. However, in spite of this treatment it fluoresced so badly that the spectrum was only obtainable by the use of strong filters. We were unable to obtain any results from this sample in the vapor phase because of the strong fluorescence.

The second sample of heavy water which we used had a $d_{20}^{20}=1.073$, which should contain on a basis of pure probability approximately 11.5 percent H_2O, 45.0 percent HDO and 43.5 percent D_2O. This sample was much better than

* Presented by K. D. Larsen in partial fulfillment of the requirements for the degree of Ph.D. at the Pennsylvania State College.

[1] D. H. Rank, J. Chem. Phys. **1**, 504 (1933).

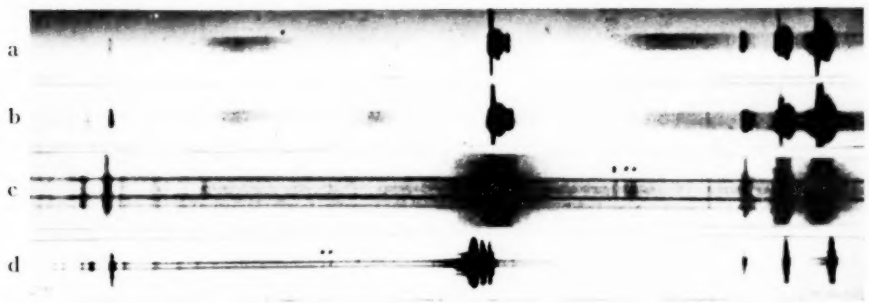

FIG. 1a, Raman spectrum of liquid H_2O; b, liquid heavy water $d_{20}^{20}=1.048$; c, Raman spectrum of H_2O vapor; d, Raman spectrum of heavy water vapor $d_{20}^{20}=1.073$. These spectra have been taken with several different spectrographs and are enlarged so as to make the mercury lines approximately correspond.

the previous one and we were able to obtain the modified lines from it. However, there was still a considerable amount of fluorescence. The heavy water was removed from the scattering tube and sealed in an ampule with a quantity of $KMnO_4$ and held at a temperature of 100°C overnight. After a distillation from the $KMnO_4$ the material was pure enough to yield a spectrum which was practically free from fluorescence.

Numerous plates were obtained by using from one to four prisms in the dispersing train. The best plates were obtained by using four prisms which gave a dispersion of 40A/mm at λ4500 and 27A/mm at λ4200. The entire spectrograph is installed in a constant temperature room, the temperature of the prisms being held constant to ±0.1°C. The time of exposure varied from 3 to 7 days with the highest dispersion used. Any lines which did not appear on the 7-day exposure could not have been made to appear upon longer exposure because of the increasing background from the unmodified scattering and unavoidable parasitic light from the scattering tube. A 3-day exposure showed two Raman lines which were excited by λ4047. The mean of all the measurements for these two lines yielded a $\Delta\nu=2666$ cm$^{-1}\pm3$ cm^{-1} and $\Delta\nu=2718$ cm$^{-1}\pm3$ cm^{-1}, respectively, for these shifts, their intensity being approximately in the ratio of 3 to 2, the 2666 shift being the stronger. A reproduction of one of the plates showing these lines appears in Fig. 1d, the Raman lines being indicated by means of ink dots below the spectrum. These results had been reported by one of us[2] previously. The longer exposures were made in an attempt to find a line in the region $\Delta\nu=3700$ cm^{-1} which one would expect from the work of Wood[3] on liquid heavy water. This particular shift falls in an unfavorable place for observation by λ4047 excitation because of the presence of a number of weak mercury lines in this region. However, by λ3650 excitation this line should fall in a place which is quite favorable for its observation. We have been unable to find this line and it seems safe to say that if this particular line appears in the spectrum of the vapor it must be considerably weaker than the other two lines which do appear. A vapor pressure of about two atmospheres was maintained in the scattering tube for all these exposures.

It appeared to be worth while to obtain more accurate measurements on the modified lines in the spectrum of H_2O, since the dispersion used in the present work was double that used in the earlier work. It had also been noted in the previous work that all the Raman lines were somewhat broader than a sharp mercury line. A 15-hour exposure with H_2O in the scattering tube showed the 3650 cm^{-1} shift excited by λ3650 to consist of a close pair of lines of equal intensity. The measurements yielded $\Delta\nu=3646.1$ cm$^{-1}\pm1.5$ and 3653.9 cm$^{-1}\pm1.5$ for these shifts, respectively. The definition on this plate was particularly good and this doublet was clearly resolved. An attempt was made to resolve the corresponding line shifted from λ3654. Since this line is considerably weaker than λ3650 several days' exposure was necessary to photograph it

[2] D. H. Rank and G. H. Fleming, Florida Meeting Am. Chem. Soc.

[3] R. W. Wood, Phys. Rev. **45**, 392 (1934).

properly and unfortunately the definition could not be maintained as sharp for the longer period of time. The third member of the triplet naturally could not be resolved, since the exciting line λ3663 is itself a close doublet of 0.38 Angstrom separation. This state of affairs would contract the pattern to an extent far beyond the photographic resolving power of the spectrograph.

Discussion

The Raman spectrum of liquid water has been obtained by numerous investigators. This spectrum is characterized by an extremely broad diffuse band whose center lies approximately 3445 cm^{-1} from the exciting line. The Raman spectrum of the vapor consists of a sharp line ($\Delta\nu = 3650$ cm^{-1}) in contrast to the band observed in the liquid. Shifting of the center of the bands in the liquid to lower frequencies compared to those observed for the vapor, is well known from work on the infrared spectrum of water.[4] The infrared spectrum of water vapor shows these bands, which have been analyzed by Mecke and his co-workers[5, 6, 7] to exhibit the structure predicted from the theory developed by Kramers,[8] Dennison[9] and Nielsen.[10] In the liquid state these infrared absorption bands no longer show this "many lined" fine structure but appear to be continuous.[4] The reason for this phenomenon is probably to be found in the action of the stray fields of neighboring molecules on the absorbing molecules in such a manner that the energy levels are no longer discrete. This phenomenon is quite marked in the Raman spectrum of liquid H_2O, HDO and D_2O, while the spectrum of liquid CS_2 apparently yields quite sharp lines.[11] From the work of Wood[3] on the liquid it is interesting to note, that the shift of the center of the band to lower frequencies in the spectrum of liquid D_2O compared to the line observed in the spectrum of the vapor, when compared to the effect observed for H_2O, appears to be proportional to the frequency.

Table I.

	H_2O			HDO			D_2O		
	$\nu(\sigma)$	$\nu(\pi)$	$\delta(\pi)$	$\nu(\sigma)$	$\nu(\pi)$	$\delta(\pi)$	$\nu(\sigma)$	$\nu(\pi)$	$\delta(\pi)$
Mecke[5]	3756	3600	1595						
Johnston and Walker[12]		3655	1648						
Rank[1]	3804	3650							
Rank		3646.1							
Larsen					2718			2666	
Bordner		3653.9							
Wood[3]		3445*		3500*	2623*			2517*	

* These values are obtained from the spectrum of the liquid and must not be compared with the values obtained from the vapor. Due to the well-known broad diffuse character of these bands the measurements obtained from the spectrum of the liquid cannot be of comparable accuracy with those obtained from the spectrum of the vapor.

In Table I we have arranged the available data on the infrared and the Raman spectrum of both ordinary and heavy water.

Mecke's[5] analysis of the infrared absorption bands of H_2O vapor leads to the values for the fundamentals given in Table I. $\nu(\sigma)$ and $\delta(\pi)$ appear as fundamentals in the infrared absorption spectrum. However, $\nu(\pi)$ makes its appearance only in the combination bands. In the Raman spectrum $R\nu(\pi)$ is observed by the appearance of a line $\Delta\nu = 3650$ cm^{-1}. A line $\Delta\nu = 3804$ cm^{-1} has been observed[1] which (though somewhat doubtful) might be correlated with $R\nu(\sigma)$. It is observed from the infrared data that $\nu(\sigma) - \nu(\pi) = 156$ cm^{-1} while from the Raman effect $R\nu(\sigma) - R\nu(\pi) = 154$ cm^{-1}. This agreement which is well within experimental error may be significant. The answer to the discrepancy between the absolute value of $R\nu(\pi)$ and $\nu(\pi)$ is probably to be found in the rotational structure of the spectrum. It is difficult to see how the Raman frequencies can be correlated with Q branch lines as is the case in diatomic molecules.*

[4] Schaefer and Matossi, *Das Ultrarote Spektrum*, p. 242.

[5] R. Mecke, Zeits. f. Physik **81**, 313 (1933).

[6] W. Baumann and R. Mecke, Zeits. f. Physik **81**, 445 (1933).

[7] K. Freudenberg and R. Mecke, Zeits. f. Physik **81**, 465 (1933).

[8] H. A. Kramers and G. P. Ittman, Zeits. f. Physik **53**, 553 (1929).

[9] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

[10] H. H. Nielsen, Phys. Rev. **38**, 1432 (1931).

[11] R. W. Wood and George Collins, Phys. Rev. **42**, 386 (1932).

* The apparent absence of a Q branch was noted by Langseth and Nielsen (A. Langseth and J. Rud Nielsen, Zeits. f. physik. Chemie **B19**, 427 (1932)) in the Raman spectrum of gaseous CO_2. They interpreted the lines which they found as maxima of P and R branches. Nielsen (Phys. Rev. **44**, 911 (1933)) has calculated the intensities of the Raman lines associated with this transition. However, the calculations do not explain the difficulty since they show that the Q branch should be considerably stronger than the P and R branches.

The observation in the present work that $R\nu(\pi)$ consists of a close pair of lines enables us to attempt an empirical explanation of the apparent discrepancy noted above. If we assume that $R\nu(\sigma)$ also consists of a close pair of lines, we find from the infrared data of Mecke that the mean of the two transitions

$$(2_{-2}\rightarrow 1_{-1}=3802.6\ \text{cm}^{-1},\quad 2_0\rightarrow 1_1=3807.9\ \text{cm}^{-1})$$

in the R branch of the 1,0,0 band yields a value of 3805.2 cm^{-1}, which is in excellent agreement with the value found for $R\nu(\sigma)$ (3804 cm^{-1}). The corresponding transitions in the 0,0,1 band would yield a value the mean of which is 1646.7 cm^{-1}, which would be in good agreement with the line $\Delta\nu=1648$ cm^{-1} found by Johnston and Walker.[12] The doublet separation in this case would be 10.3 cm^{-1}. Unfortunately the rotational constants are not available for the 0,1,0 band. If we assume them to be sensibly the same as in the 1,0,0 band the value obtained for the mean of the corresponding transitions in the 0,10, band would be 3649.0 cm^{-1} in excellent agreement with the value found for $R\nu(\pi)$ (3649.5 cm^{-1}). However, if the same rotational constants were used as in the 1,0,0 band the doublet separation would be too small by about 30 percent to check the observed value (7.8 cm^{-1}).

If the numerical agreement using the empirical assignment outlined above, for the observed Raman transitions, is not fortuitous the selection rules for the rotational quantum numbers would appear to be $J\rightarrow J-1$, $K\rightarrow K+1\neq 0$. (These selection rules as stated would correspond to anti-stokes transitions.) The rule $K+1\neq 0$ would explain the absence of the $1_{-1}\rightarrow 0$ transition. If the $K+1\neq 0$ rule did not apply one would obtain a triplet for the $2\rightarrow 1$ transitions instead of the observed doublet. Unfortunately the transitions involving higher values of J, excited by λ3650 would be masked by the $2\rightarrow 1$ transitions excited by λ3654 and λ3663. λ2536 excitation would remove the experimental difficulties cited above and enable one to obtain these higher transitions providing they appear with appreciable intensity.

We wish to acknowledge our indebtedness to Mr. G. H. Fleming of the Chemistry Department for his assistance in the preparation of the heavy water.

Note added in proof:

Since this paper was written a communication has appeared by R. W. Wood[13] in which he gives 2601 and 2674 cm^{-1} for the Raman frequencies of D_2O and HOD vapors, respectively. The values given in the present were obtained using much higher dispersion and should accordingly be considerably more accurate.

[12] H. L. Johnston and M. K. Walker, Phys. Rev. **39**, 535 (1932). It is a curious fact that this transition does not appear in the Raman spectrum of the liquid. Professor Wood[3] using λ2536 excitation did not obtain it either for H_2O or D_2O. λ2536 excitation should be quite favorable for the observation of this frequency because of the absence of other exciting lines. One of us[1] previously was unable to find this transition in the spectrum of the vapor.

[13] R. W. Wood, Phys. Rev. **45**, 732 (1934).

The Equilibrium $H_2O+HD=HOD+H_2$ and Its Rôle in the Separation of the Hydrogen Isotopes

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WHENEVER hydrogen is liberated from an aqueous solution containing heavy water a separation of the isotopes occurs, i.e., the isotopic composition of the gas is not the same as that of the liquid.

To interpret this behavior the following equilibria have to be taken into consideration.

$$H_2+D_2\rightleftarrows 2HD \quad (1)$$

$$H_2O+D_2O\rightleftarrows 2HOD \quad (2)$$

$$H_2O+HD\rightleftarrows HOD+H_2. \quad (3)$$

These equations define the D-content of hydrogen evolved from a solution of given D-content under equilibrium conditions.

To simplify the treatment we will take the relative concentrations of the molecular species H_2, HD, D_2, H_2O, HOD, and D_2O to be the same in the liquid and in the gas phase, i.e., we will neglect the difference in the vapor pressure of light and heavy water and the possible difference in the solubility of light and heavy hydrogen.

The equilibrium constant of the reaction (1) is well known theoretically[1] and experimentally[2, 3] and is $K_1=(HD)^2/(H_2)(D_2)=3.27$ at 20°C. The equilibrium constant $K_2=(HDO)^2/(H_2O)(D_2O)$ has been calculated by Topley and Eyring[4] to be 3.27 at 20°C. Both K_1 and K_2 are nearly independent of temperature.

According to Bonhoeffer and Rummel[5] K_3 is 3.8 at 20°. We have also obtained the same value at this temperature and about 2 at 100°C.[6]

In a number of processes when hydrogen is evolved from aqueous solutions we could actually observe that the establishment of these equilibria does in fact occur and is, in these cases, the only cause for the separation of the hydrogen isotopes: the observed "separation factor" defined by

$$s=\frac{\text{H-content in the hydrogen}}{\text{D-content in the hydrogen}}:\frac{\text{H-content in water}}{\text{D-content in water}}$$

is practically equal to the equilibrium constant K_3. (As a simple calculation shows s would be identical with K_3 if $K_1=K_2=4$.)

Some examples of such processes are (1) the electrolysis of water,[7] (2) the decomposition of sodium formate by palladium black or *B. coli*,[8] (3) the evolution of hydrogen from water by the reaction $K_4Co(CN)_6+H_2O=K_3Co(CN)_6+KOH+\frac{1}{2}H_2$.[9]

In the case of electrolysis this equilibrium is not always established but only under certain conditions, e.g., on activated platinum electrodes.

The separation for the hydrogen isotopes according to the equilibria (1), (2) and (3) will furthermore occur when a mixture of light and heavy steam is decomposed at high temperatures, e.g., with iron or in the water-gas reaction or when oxides such as CuO are reduced by hydrogen. At temperatures when all the components H_2, HD, D_2, H_2O, HOD and D_2O are present together (in equilibrium) a sample on removal from the reaction chamber will reveal an isotopic fractionation since in general the concentration of D in the water molecules will not be equal to that in the hydrogen.

It is obvious also that in other cases when the establishment of the equilibria (1), (2) and (3), especially that of (3) [the equilibrium defined by (2) is always established in the liquid] is not

[1] Urey and Rittenberg, J. Chem. Phys. **1**, 137 (1933).

[2] Rittenberg, Bleakney and Urey, J. Chem. Phys. **2**, 48 (1934).

[3] A. and L. Farkas, Nature **132**, 894 (1933); Proc. Roy. Soc. **A144**, 467 (1934).

[4] Topley and Eyring, J. Chem. Phys. **2**, 217 (1934).

[5] Bonhoeffer and Rummel, Naturwiss. **22**, 45 (1934); Zeits. f. Elektrochem. (in print).

[6] A. and L. Farkas, Proc. Roy. Soc. **A**. (1934) (in print).

[7] A. and L. Farkas, Proc. Roy. Soc. **A** (1934) in print.

[8] Farkas, Farkas and Yudkin, Proc. Roy. Soc. **B** (1934) in print.

[9] This experiment was suggested to us by Dr. J. Weiss and is of some interest since the liberation of hydrogen takes place from the homogeneous liquid.

attained as for instance in electrolysis in general or in the dissolution of metals in water or in acids[10–13] the exchange reaction

$$H_2O+HD\rightleftharpoons HOD+H_2$$

may be operative to a certain extent thus modifying the primary separation of the hydrogen isotopes caused, e.g., in the electrolysis, by the different rate of discharge of the H^+ and D^+ ions or by the different rate of recombination of the H and D atoms.

It is hard to tell the extent of this exchange reaction in a particular case. That it really exists is shown by the fact that even the exchange between molecular hydrogen and water is catalyzed by different substances especially by metals.[14] This reaction is also clearly operative, e.g., on the surface of a metal electrode or on the surface of other metals since the high reactivity of hydrogen in nascent state is well known.

Qualitatively we can state that when the evolved gas contains more light hydrogen than is defined by the concentration determined by the equilibrium constant K the primary separation of the hydrogen isotopes is larger than the observed separation factor since the equilibrium reaction

$$H_2O+HD\rightleftharpoons HDO+H_2$$

tends to bring about a separation factor equal to K_3. On the other hand if the D-content of the gas liberated is higher than determined by the equilibrium the primary separation will be still smaller than the observed. The former behavior is shown when metals, such as zinc, iron, etc., are dissolved in dilute acids or in the electrolysis of water, the latter in the dissolution of alkalis or alkaline earths in water. It is thus clear that the rate-determining steps are different in these processes since the separation factor in one of them is smaller, in the other, larger than the equilibrium constant.[15]

In this connection it may be pointed out that for the natural distribution of light and heavy hydrogen such equilibria between hydrogen compounds will play an important rôle. Natural hydrogen should have a D-content 1 : 15,000 to 1 : 20,000[16] and also other hydrogen compounds will reveal a different D-content compared with water. Halford, Anderson and Bates[17] have shown that the equilibrium constant of the exchange reaction between heavy water and acetone

$$CH_3COCH_3+HOD=CH_3COCH_2D+H_2O$$

is about 2, i.e., the heavy hydrogen is preferentially present in the acetone. It is most probable that this is also true for other organic compounds and this circumstance may explain the fact that water obtained from vegetable or animal material proves to be "heavy" compared with water.[18]

We are very much indebted to Professor E. K. Rideal, F.R.S. for his interest in our work and to the Central British Fund for German Jewry for a financial grant.

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[10] A. and L. Farkas, Nature **133**, 139 (1934). Proc. Roy. Soc. **A144**, 16 (1934).

[11] Hughes, Ingold and Wilson, Nature **133**, 291 (1934), J. Chem. Soc. **1934**, 493.

[12] Horiuti and Szabo, Nature **133**, 327 (1934).

[13] Davis and Johnston, J. Am. Chem. Soc. **56**, 492 (1934).

[14] Horiuti and Polanyi, Nature **132**, 819 (1933).

[15] Discussion on heavy hydrogen held in The Chemical Soc. London, May 17, 1934. E. K. Rideal and A. Farkas.

[16] Bradley and Urey (Phys. Rev. **40**, 889 (1932)), have found that the D-content of hydrogen from He-bearing natural gases is the same as of normal water. Obviously this hydrogen was not in equilibrium with water.

[17] Halford, Anderson and Bates, J. Am. Chem. Soc. **56**, 491 (1934).

[18] Emeleus, James, King, Pearson, Purcell and Briscoe, J. Chem. Soc. London, in print.

The Infrared Absorption of Solutions of Hydroxides and Hydrolyzing Salts

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(Received May 21, 1934)

Absorption bands have been found at 3.65μ and 5.2μ in aqueous solutions of NaOH, KOH and LiOH. Solutions of $ZnCl_2$, $ZnBr_2$, $NH_4C_2H_3O_2$, Na_2CO_3, $NaC_2H_3O_2$, $Na_2B_4O_7$, Na_2SiO_3 and $Al_2(SO_4)_3$ were studied in the region from 2.8μ to 6μ and bands were observed at about 3.45μ, 4.5μ, 5.2μ and 5.6μ. The solutions which are acid in reaction had intense bands at 3.6μ and 5.2μ, while the basic solutions gave a strong band at 5.6μ. This variation in intensity indicates that the absorption bands are due to undissociated molecules bound to water molecules. The band at 4.5μ is probably due to water which has been modified by the ions. The hydroxides showed the absorption bands at 3.6μ and 5.2μ when 0.1N solution was used.

GRANTHAM[1] measured the absorption of several hydroxides in aqueous solutions from 1μ to 3μ and found an intense band at 2.29μ for all the solutions except NH_4OH which had the maximum of absorption at 2.20μ. tions and found that the intensity of the water absorption was changed. Small bands occurred at 0.96μ, 1.10μ, and 1.27μ for all the hydroxides in alcoholic solutions and these bands were thought to be due to the OH ion.

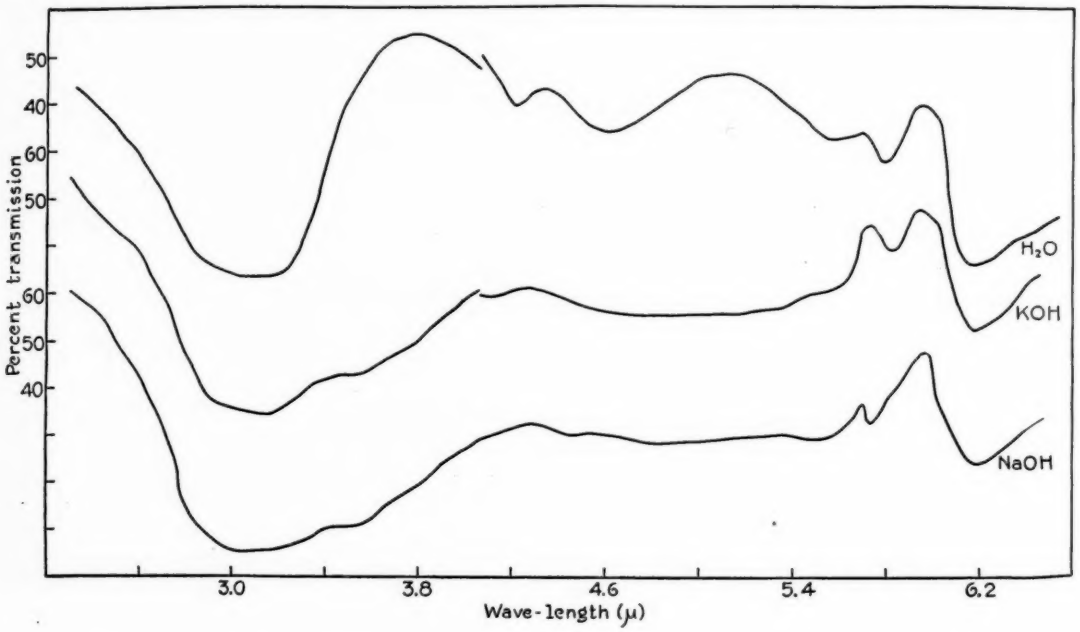

FIG. 1. The percent transmission of water and of NaOH and KOH solutions from 2.8μ to 6.6μ.

Because the absorption bands had the same wave-length Grantham concluded that the absorption was due to the OH ions. Collins[2] also measured the absorption of hydroxides in solutions and found that the intensity of the water absorption was changed. Small bands occurred at 0.96μ, 1.10μ, and 1.27μ for all the hydroxides in alcoholic solutions and these bands were thought to be due to the OH ion.

These bands appear to be part of a harmonic series which has a fundamental in the long wave-length region. The present work was undertaken to look for such bands and the region from 2.8μ to 6.5μ was studied. The measurement of the absorption bands was done in a way similar to

[1] G. E. Grantham, Phys. Rev. **18**, 339 (1921).
[2] J. R. Collins, Phys. Rev. **20**, 486 (1922).

that employed by Plyler and Barr.[3] In Fig. 1 is shown the percent transmission of H_2O and 7.5N NaOH and 7.5N KOH solutions. In the region of 4.2μ the spectrometer slits were changed and this caused breaks in some of the curves. The cell thickness was approximately 0.01 mm for each solution. The transmission is less than is found for water. In Fig. 2 the ratio of the percent transmission of the solutions to that of water is plotted. Intense bands are shown in the regions of 5.20μ and 3.65μ.

A 5N solution of LiOH also gives the same bands. In the region of 3.65μ the bands appear to be double with a less intense component on the long wave-length side. On account of the rapid change in the coefficient of absorption of water, it was difficult to determine the true shape or position of this band. The small band in the region of 4.2μ was not found in all determinations and may be due to observational

[3] E. K. Plyler and E. S. Barr, J. Chem. Phys. (in press).

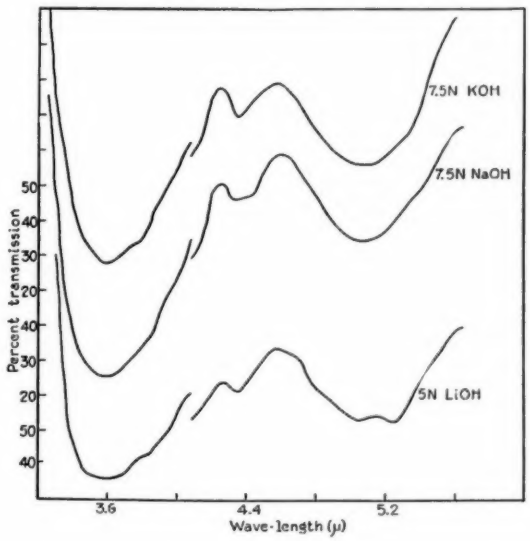

FIG. 2. The ratio of the transmission of solutions of KOH, NaOH, and LiOH as compared to water.

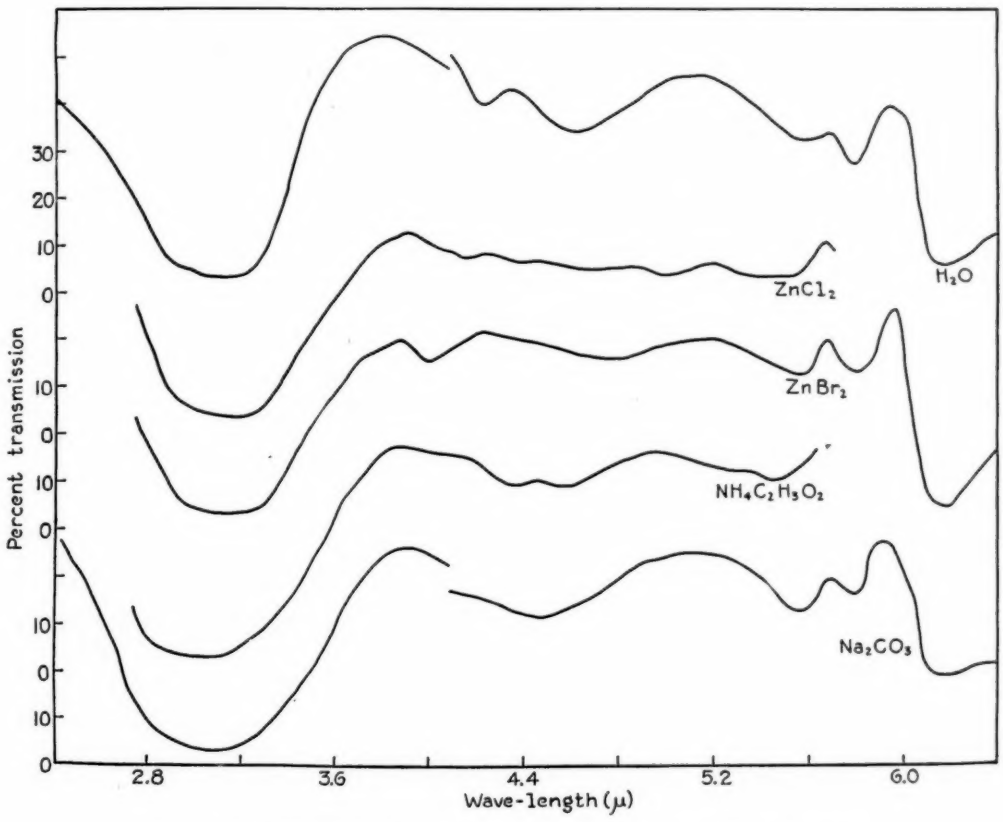

FIG. 3. The percent transmission of some hydrolyzing salts from 2.8μ to 6.6μ.

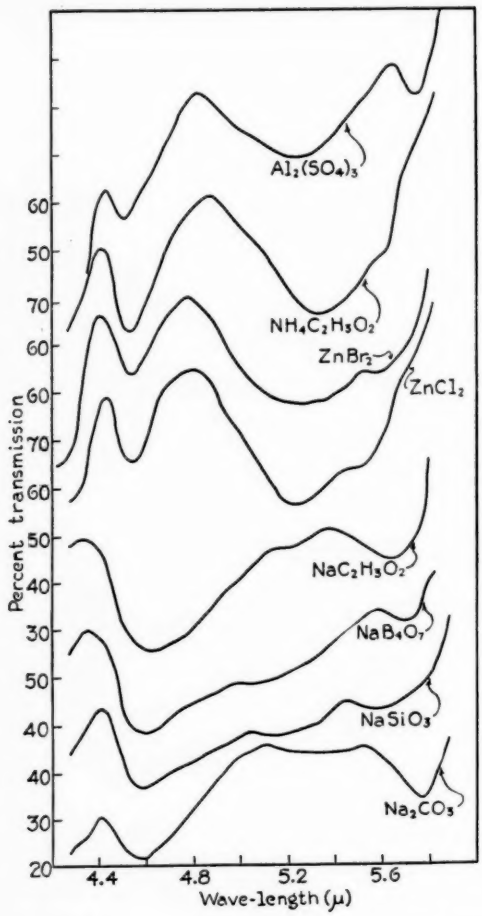

FIG. 4. The percent transmission of some hydrolyzing salts compared with water from 4.2μ to 6.0μ. (The curve labelled NaB_4O_7 should be $Na_2B_4O_7$; the curve $NaSiO_3$ should be Na_2SiO_3.)

errors. There is a strong band in this region due to CO_2 in the atmosphere and the deflections of the galvanometer are greatly reduced.

The bands reported by Collins[2] agree in position with harmonics of these bands. If the 3.65μ band is called ν_1, and the 5.2μ band ν_2, then $3\nu_1$ corresponds to 1.27μ and $4\nu_1$ to 0.95μ and $5\nu_2$ corresponds to 1.05μ. The combination of $\nu_1+\nu_2$ corresponds to a band at 2.3μ. This agreement is not very satisfactory as the observed band occurs at 2.2μ. By a study of hydrolyzing salts in this region it has been found that the 2.2μ band is a fundamental frequency and not a combination band.

A study of hydrolyzing salts was next made to see if the hydroxides formed in this way had bands at 3.65μ and 5.2μ. Solutions of 10N $ZnCl_2$, 10N $ZnBr_2$, 10N $NH_4C_2H_3O_2$ and 2.5N Na_2CO_3 were measured from 2.8μ to 6.6μ and the results are shown in Fig. 3. The percent transmission in this region is much less than that of water. The acid solutions have less transmission at 3.45μ and 5.2μ than the basic solutions but the basic solutions have less transmission at 5.6μ. This variation in intensity is readily seen when the ratio of the percent transmission of the solution compared to water is plotted. The results for the region from 4μ to 6μ are shown in Fig. 4. The first curves are for acid solutions and the band at about 5.6μ, which is characteristic for all acid solutions,[3] is very weak. The band at 5.2μ, which has been found for all hydroxides, is intense. As an acid solution of a hydrolyzing salt indicates more H ions than OH ions, the 5.6μ acid band must be due to the

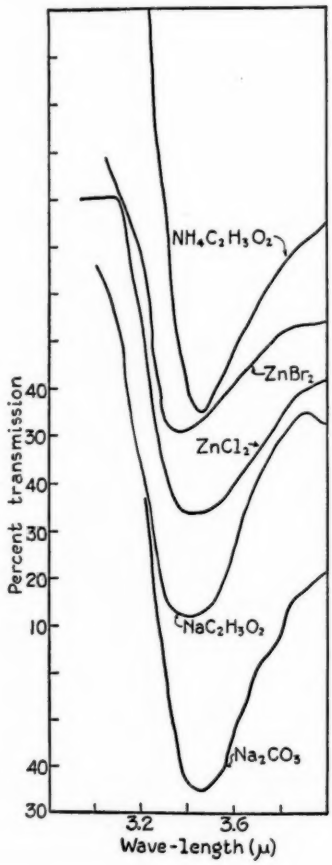

FIG. 5. The percent transmission of some hydrolyzing salts compared with water from 2.8μ to 4μ.

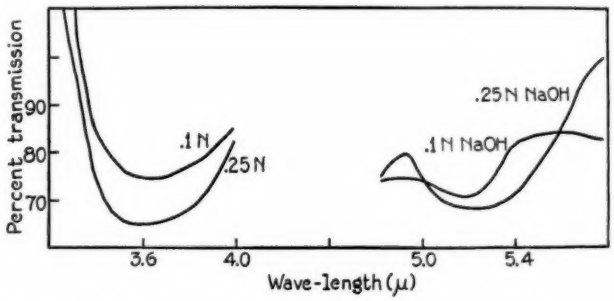

FIG. 6. Intensity of the hydroxide bands at 3.65μ and 5.2μ as affected by concentrations.

undissociated acid molecule attached to one or more water molecules and the 5.2μ band due to the undissociated hydroxide molecule attached to one or more water molecules. The four lower curves in Fig. 4 show the percent transmission of 7N $NaC_2H_3O_2$, 0.5N $Na_2B_4O_7$, 5N Na_2SiO_3, 2.5N Na_2CO_3 which are basic. The 5.6μ acid band is intense and the 5.2μ hydroxide band is weak. This result also shows that these bands are due to the undissociated molecule. Because of the strong hydroxide band at 5.2μ, the bands produced by the acids at 5.6μ are somewhat distorted. The $NH_4C_2H_3O_2$ solution acts similarly to acid solutions but this result may be produced by the absorption due to the NH_4 ion in the region of 5.2μ.

Intense bands were found for all the hydrolyzing salts in the region of 4.5μ. These bands are not present in the solutions of acids or hydroxides and are to be attributed to energy levels characteristic of hydrolyzing salts. A strong absorption band is found in this region in all crystals having water of crystallization and it is possible that some of the water molecules of the solution are bound between the ions in a similar way to water in crystals. In Fig. 5 are shown the results for solutions of $NH_4C_2H_3O_2$, $ZnBr_2$, $ZnCl_2$, $NaC_2H_3O_2$ and Na_2CO_3 in the region from 2.8μ to 4μ. On account of the low transmission of water in this region, the position of the band could not be found so accurately. However, it was readily found that this region had an intense band at about 3.45μ.

The hydroxide bands at 3.65μ and 5.2μ have been found to arise in energy changes between the undissociated hydroxide molecule and one or more water molecules. Measurements were made on concentrations from 10N to 0.1N to see if the bands decreased rapidly in intensity as the concentration decreased. The intensity appeared to vary directly as the concentration and the bands were still present with 0.1N solutions. Curves for 0.1N and 0.25N solutions of NaOH are shown in Fig. 6.

The hydroxide solutions have been studied[4] by means of the Raman spectra and shifts have been found which correspond to a band with a frequency of 3600 cm^{-1}. Neither of the bands at 3.65μ or 5.2μ was observed.

The intensity of the bands at 3.45μ, 5.2μ and 5.6μ is a measure of the hydration for the given concentration. Because of the thin cells it is difficult to obtain quantitative results. However, the harmonics of these bands, which occur in the region of 2μ, could be used to determine the degree of hydration. A study of this type has been made by Krishnamurti[5] by the use of the Raman effect. He did not find any shifts which correspond to the bands observed in this work.

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[4] L. A. Woodward, Phys. Zeits. **32**, 261 (1931).
C. C. Hatley and Dixon Callihan, Phys. Rev. **38**, 909 (1931).

[5] P. Krishnamurti, Ind. J. Phys. **6**, 345 (1931).

The Quantum Mechanics of Unsaturated and Aromatic Molecules: A Comparison of Two Methods of Treatment

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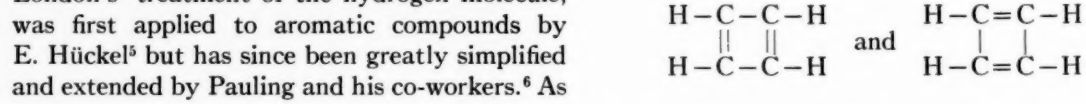
(Received June 11, 1934)

A comparison is made of two quantum-mechanical methods of treatment of unsaturated and aromatic organic molecules. The HLSP treatment, which is based upon the use of Slater valence-bond eigenfunctions, seems to give results in somewhat better general agreement with experiment than the HMH, which is based upon the use of molecular orbitals of the Hund-Mulliken type. The latter, however, can be extended to a wider variety of problems. The problems considered include the energy relations among hydrocarbons, the dissociation of aryl substituted ethanes, the electron-affinity of free radicals and the acid strength of hydrocarbons.

FOR the quantum-mechanical treatment of the problems connected with molecular structure, there have been devised two methods of attack which differ somewhat in the nature of the approximations introduced. In a number of cases for which calculations have been made, these have been found to lead to results which agree quite well with each other in a general sort of way but which disagree, nevertheless, in some rather important particulars. Slater[1] has treated this question in some detail, with special reference to the metals and to the hydrogen molecule and Van Vleck[2] has done the same for methane. In this paper I wish to extend the discussion to several types of unsaturated and aromatic organic molecules.

THE HEITLER-LONDON-SLATER-PAULING (HLSP) METHOD

This method, which was developed originally by Slater[3] as a generalization of Heitler and London's[4] treatment of the hydrogen molecule, was first applied to aromatic compounds by E. Hückel[5] but has since been greatly simplified and extended by Pauling and his co-workers.[6] As an illustration we shall take the simple case of cyclobutadiene, C_4H_4. (The extension to more complicated systems will be obvious. For a detailed discussion of the method, the reader is referred to the original articles.) Each carbon atom will be considered to have one $2s$ and three $2p$ orbital functions, occupied by one electron each. Of these, the $2s$ and two of the $2p$ functions are used up in forming single bonds to the two adjacent carbon atoms and to the attached hydrogen atom. The remaining $2p$ function, which projects at right angles to the plane of the ring, is then free to combine with the corresponding functions on the other carbon atoms. Only these last interactions need be considered, since the neglect of the others affects merely the position of the arbitrarily chosen zero point of the calculation. Thus the problem becomes one of four electrons only. For the molecule there are then the two "canonical" structures



for which the corresponding Slater valence-bond eigenfunctions can be set up in the usual way. The secular equation is

$$\begin{vmatrix} Q+\alpha-W & \frac{1}{2}Q+2\alpha-\frac{1}{2}W \\ \frac{1}{2}Q+2\alpha-\frac{1}{2}W & Q+\alpha-W \end{vmatrix} = 0,$$

as is easily shown, either by the procedure given by Pauling[6] for calculating the matrix elements,

[1] J. C. Slater, Phys. Rev. **35**, 509 (1930).

[2] J. H. Van Vleck, J. Chem. Phys. **1**, 177, 219 (1933); **2**, 20 (1934).

[3] J. C. Slater, Phys. Rev. **38**, 1109 (1931).

[4] W. Heitler and F. London, Zeits. f. Physik **44**, 455 (1927).

[5] E. Hückel, Zeits. f. Physik **70**, 204 (1931).

[6] L. Pauling, J. Chem. Phys. **1**, 280 (1933); L. Pauling and G. W. Wheland, ibid. **1**, 362 (1933); L. Pauling and J. Sherman, ibid. **1**, 679 (1933).

or by the one given by Eyring and Kimball.[7] In this equation Q is the coulomb integral $(\psi_1\psi_2\psi_3\psi_4|\mathrm{H}|\psi_1\psi_2\psi_3\psi_4)$, α is the single exchange integral between adjacent carbon atoms $(\psi_1\psi_2\psi_3\psi_4|\mathrm{H}|\psi_2\psi_1\psi_3\psi_4)$, and ψ_i is the $2p$ function on the ith carbon atom. Here the single interchange integrals of the energy between non-adjacent atoms, all multiple interchange integrals, and all interchange integrals of unity have been neglected. The solutions of the secular equation are $W=Q+2\alpha$, $Q-2\alpha$, of which the former represents the ground state, since α is presumably negative. It will be convenient to eliminate Q from the problem by considering not the total energy $Q+2\alpha$, but merely the resonance energy, which is the difference between this quantity and the energy of a single one of the two equivalent "Kekulé-like" structures with alternating single and double bonds. This gives: Resonance energy $=Q+2\alpha-(Q+\alpha)=\alpha$.

The Hund-Mulliken-Hückel (HMH) Method

This method, which has been used with considerable success by Hund,[8] Mulliken,[9] Lennard-Jones,[10] Herzberg,[11] Dunkel,[12] Bloch[13] and others in treating a wide variety of problems, has also been extended to the unsaturated and aromatic compounds by Hückel.[5, 14] The following discussion follows his treatment quite closely, except for a slight modification in the nomenclature. Again let us use cyclobutadiene as an example. As before, the problem is limited to a consideration of the interactions of the $2p$ functions (one for each carbon atom) projecting at right angles to the plane of the ring. Instead of setting up valence-bond eigenfunctions, however, we shall consider each electron moving alone in a Hartree self-consistent field, which is produced by the nuclei and by all the electrons other than itself and which possesses the symmetry of the nuclei. The eigenfunction for a single electron can then be represented by a linear combination of the functions $\psi_1\cdots\psi_4$ and the corresponding secular equation is

$$\begin{vmatrix} q-W & \beta & 0 & \beta \\ \beta & q-W & \beta & 0 \\ 0 & \beta & q-W & \beta \\ \beta & 0 & \beta & q-W \end{vmatrix} = 0,$$

where q is the coulomb integral $(\psi_i|H'|\psi_i)$, β is the resonance integral $(\psi_i|H'|\psi_{i\pm1})$, with $i=1$, 2, 3, 4 and H' is the Hamiltonian operator corresponding to the self-consistent field. The resonance integrals between non-adjacent carbon atoms and all resonance integrals of unity have been neglected. The solutions of the equation are:

$$\begin{aligned} W &= q+2\beta\cos(2\pi j/4) \qquad (j=0,\,1,\,2,\,3) \\ &= q+2\beta,\ q,\ q-2\beta,\ q. \end{aligned}$$

Of these roots, $q+2\beta$ is the lowest, since β is presumably negative, and consequently two of the electrons are assigned to the corresponding eigenfunction, one with positive and one with negative spin. The other two electrons are then assigned to the eigenfunction corresponding to the next lowest root, q. On account of the degeneracy of this root, however, the assignment can be made in various ways, and hence the ground state of the molecule is degenerate; there are in fact one triplet and three singlet terms, all with energy $2(q+2\beta)+2q=4q+4\beta$. In this treatment the interactions between the electrons have been neglected, except insofar as they are taken care of by the self-consistent field.

It is again convenient to eliminate the integral q from the problem by subtracting from the total energy, $4q+4\beta$, the energy of a single "Kekulé-like" structure, which can readily be shown to be $4q+4\beta$. Thus according to this treatment, cyclobutadiene has zero resonance energy—a result in poor agreement with the value, α, found by the HLSP method.

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[7] H. Eyring and G. E. Kimball, J. Chem. Phys. **1**, 239 (1933).

[8] F. Hund, Zeits. f. Physik **73**, 1 (1931); **73**, 565 (1932).

[9] R. S. Mulliken, J. Chem. Phys. **1**, 492 (1933) and further references given there.

[10] J. E. Lennard-Jones, Trans. Faraday Soc. **25**, 668 (1929).

[11] G. Herzberg, Zeits. f. Physik **57**, 601 (1929).

[12] M. Dunkel, Zeits. f. physik. Chemie **B7**, 81; **10**, 434 (1930).

[13] F. Bloch, Zeits. f. Physik **52**, 555 (1928).

[14] E. Hückel, Zeits. f. Physik **72**, 310 (1931); **76**, 628 (1932); **83**, 632 (1933); Trans. Faraday Soc. **30**, 40 (1934).

General Comparison of the Two Methods

It is readily seen that the HMH procedure is the less rigorous of the two, since it does not take proper account of the Pauli exclusion principle. As Van Vleck[2] has pointed out, this results in an extreme piling up of electrical charges in the molecule. In fact, for an appreciable part of the time all the electrons are located on the same carbon atom. This shows that the self-consistent field has not properly accounted for the interactions between the electrons and throws some doubt upon the validity of the procedure. It seems likely that this error will increase in importance with the size of the molecule. A more rigorous procedure would be to set up an antisymmetric linear combination, Φ, of functions which involve the molecular orbitals that result from the solution of the secular equation, and then to calculate the energy from the relation $W=(\Phi|H|\Phi)/(\Phi\Phi)$, where H is now the correct Hamiltonian operator for the actual system under consideration. This refinement would be very difficult to carry out, however, since it would introduce a number of additional integrals which could not be readily evaluated. Consequently, we shall continue to use the simpler, but less rigorous procedure originally described. As a matter of fact, the HMH treatment, even with the refinement indicated, would probably still be somewhat inferior to the HLSP. The reason for this is that then the two methods become equivalent, except for the fact that in the former each bond is considered to be half ionic and half covalent, while in the latter each bond is considered to be completely covalent. The truth undoubtedly lies somewhere between the two extremes but somewhat nearer the latter. In the analogous case of the hydrogen molecule, calculation shows that the HLSP treatment gives a better answer than the corrected HMH treatment by approximately 6 kcal.[15] Furthermore, Weinbaum[16] has found that the ratio of the ionic to the covalent terms in H_2 is approximately 1 : 4, in better agreement with the HLSP treatment than with the HMH.

From this discussion we are led to expect that the HLSP procedure will in general give results in better agreement with experiment than the HMH. Since, however, both methods are so extremely crude, it seems advisable to consider as large a number of specific examples as possible before coming to any definite conclusion.

Hydrocarbons

In Table I are collected the results of calculations for a number of unsaturated and aromatic hydrocarbons. The agreement with experiment is indicated by the constancy of the values of α and of β in the fifth and sixth columns, respectively. It will be seen that the agreement is fairly good. From the heats of hydrogenation of benzene, Hückel has derived a further estimate of $\beta=-15$ kcal. $=-0.65$ e.v., which is considerably higher than most of the values in the table, but agrees well with that found for graphite. (This last calculation was made on the assumption that the interactions between the different planes could be neglected.[17]) This variation in the values of β may result from experimental error or may indicate a defect in the method of calculation. The mutual consistency of the results obtained by the two methods is indicated by the constancy of the ratio β/α given in the last column. It will be seen that, if cyclobutadiene and cycloöctatetraene are left out of account, the extreme variation is only from 0.477 to 0.555, which is no larger than might be expected in view of the different nature of the approximations made in the two cases.

The discrepancies in the cases of cyclobutadiene and cycloöctatetraene need to be considered in some detail. Hückel considered that the HMH treatment was the more reliable since it seemed to account more definitely for the instability of the four and eight membered rings, as compared with benzene but it is doubtful if his conclusion is justified. If the interactions between the electrons were properly considered, the calculated energies would be considerably altered. A careful investigation of this point, which is too involved to be given here, shows that the effect is in the proper direction and perhaps of the correct order of magnitude to bring the results of the HMH treatment into

[15] L. Pauling, private communication.

[16] S. Weinbaum, J. Chem. Phys. **1**, 593 (1933).

[17] Cf. J. E. Lennard-Jones, Trans. Faraday Soc. **30**, 58 (1934). Each bond is a double bond one-third of the time, instead of two-thirds, as stated by Lennard-Jones.

TABLE I. *Resonance energies (R.E.) of hydrocarbons.*

Compound	R.E. Empirical	R.E. HLSP	R.E. HMH	α	β	α/β
Cyclobutadiene		1.000α[e]	0.00β[d]			∞
Benzene	-1.7[a] e.v.	1.106α[e, e]	2.00β[d]	-1.5 e.v.	-0.85 e.v.	0.553
Cycloöctatetraene		1.290α[h]	1.66β[d]			0.777
Biphenyl	-3.77[a]	2.37α[b]	4.38β[d]	-1.6	-0.86	0.541
Naphthalene	-3.24[a]	2.04α[e, f]	3.68β[d]	-1.6	-0.88	0.555
Anthracene	-4.54[a]		5.32β[d]		-0.85	
Phenanthrene	-4.78[a]		5.45β[h]		-0.88	
Phenylethylene	-2.00[a]	1.31α[b]	2.42β[h]	-1.5	-0.83	0.541
Stilbene	-4.09[a]	2.59α[b]	4.88β[h]	-1.6	-0.84	0.531
Isostilbene	-3.87[a]	2.55α[b]	4.81β[h]	-1.5	-0.80	0.530
1,3,5 Triphenylbenzene	-7.9[b]	4.77α[b]	9.15β[h]	-1.66	-0.86	0.521
Butadiene		0.232α[b]	0.47β[d]			0.494
Hexatriene		0.482α[b]	0.99β[d]			0.487
Octatetraene		0.725α[b]	1.52β[d]			0.477
Graphite	-0.37[g]		0.58β[h]		-0.64	

[a] L. Pauling and J. Sherman, J. Chem. Phys. **1**, 606 (1933).
[b] L. Pauling and J. Sherman, J. Chem. Phys. **1**, 679 (1933).
[e] L. Pauling and G. W. Wheland, J. Chem. Phys. **1**, 362 (1933).
[d] E. Hückel, Zeits. f. Physik **76**, 636 (1932).
[e] E. Hückel, Zeits. f. Physik **70**, 253 (1931).
[f] Corrected value obtained by rigorous solution of the secular equation, J. Sherman, J. Chem. Phys. **2**, 488 (1934).
[g] J. Sherman, private communication. The figure gives the resonance energy per carbon atom.
[h] New calculations by present author.

agreement with those of the HLSP. Hückel argued further that the ground states of cyclobutadiene and of cycloöctatetraene are degenerate in the HMH treatment as long as the electronic interactions are neglected, while that of benzene is single, and hence that the instability of the former may be partly due to the ease with which they can be raised to higher and more reactive levels. If, however, the electronic interactions are included, the degenerate ground states are split into levels with separations of at least the same order of magnitude as that between the two lowest states of benzene.[18] It seems more likely that the correct explanation of the instability of cyclobutadiene and of cycloöctatetraene is to be found in the steric factors involved, which neither method can take into account; in the former the strain is considerable, while in the latter the large ring probably does not lie in one plane. Hence the apparent superiority of the HMH treatment in these two cases is apparently to be explained as the result of a quite fortuitous cancellation of errors.

[18] Cf. the term-diagrams given by Hückel in his first paper, reference 5, pp. 249–251.

Free radicals

Pauling and Wheland[6] have applied the HLSP and Hückel[14] the HMH procedure to the problem of the dissociation of aryl substituted ethanes into free radicals. The two treatments agree in ascribing the stability of the radicals to the fact that an increase in the resonance energy of the system after dissociation partially compensates for the energy required to break the ethane bond in the original molecule. Obviously, the degree of dissociation will be expected to increase with this extra "free radical resonance energy." In Table II are collected the results of a number of calculations for various radicals. The consistency of the results obtained by the two methods is again indicated by the constancy of the ratio of β/α given in the last column. It will be observed that the ratio is not so constant as before, varying from 0.587 to 0.927 and that it is uniformly higher than was found for the hydrocarbons (cyclobutadiene and cycloöctatetraene excepted). This discrepancy can be explained partially, although apparently not completely, on the assumption that the free radical resonance energies calculated by the HLSP method are too high, in consequence of the neglect of excited structures. It is only to

TABLE II. *Free radical resonance energies of substituted methyls.*

Radical	HLSP[a]	HMH[b]	β/α
Phenylmethyl	0.509α	0.720β	0.707
β-naphthylmethyl	0.631α	0.743β[c]	0.849
Biphenylmethyl	0.647α	0.756β[c, d]	0.856
α-naphthylmethyl	0.752α	0.811β[c]	0.927
Fluoryl	0.800α	1.343β[c]	0.596
Diphenylmethyl	0.841α	1.300β	0.647
Phenylfluoryl	1.076α	1.835β[c]	0.587
Triphenylmethyl	1.108α	1.794β	0.617
β-naphthyldiphenylmethyl	1.172α		
Biphenyldiphenylmethyl	1.174α	1.819β	0.645
Dibiphenylphenylmethyl	1.235α	1.841β	0.671
α-naphthyldiphenylmethyl	1.240α	1.856β[c]	0.668
Tribiphenylmethyl	1.291α	1.859β	0.694

[a] L. Pauling and G. W. Wheland, J. Chem. Phys. **1**, 370 (1933). Note the corrections in a number of the values which are listed at the end of this paper.

[b] E. Hückel, Zeits. f. Physik **83**, 632 (1933).

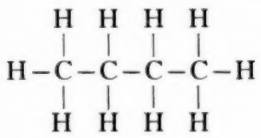
[c] New calculations by present author.

[d] For this radical Hückel gives the value of 0.897β but his calculations are apparently in error.

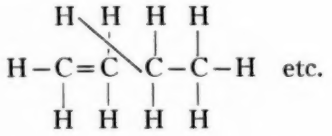
be expected, however, that the values of β/α, obtained from systems of different types, may not agree perfectly. The comparison of the calculations with experiment is rather difficult here since the experimental data are both meager and inaccurate. It is fairly certain, however, that the qualitative order of increasing dissociation is: any ethane with less than six aryl groups $\ll$diphenyldifluoryl$\ll$hexaphenylethane $<$ tetraphenyldi-β-naphthylethane $<$ tetraphenyldi-α-naphthylethane $\leqq$diphenyltetrabiphenylethane $<$hexabiphenylethane. Tetraphenyldibiphenylethane has not been included in this list since its degree of dissociation has never been measured, even approximately. It is usually estimated to lie between hexaphenylethane and tetraphenyldi-β-naphthylethane, but the present calculations indicate that this may not be correct. With this one possible exception, the HLSP treatment leads to qualitatively correct predictions in regard to all the hexa-aryl substituted ethanes, while the HMH treatment, on the other hand, is in error in the case of diphenyldifluoryl. Thus the former seems here to be definitely the more reliable, in confirmation of the considerations of a preceding paragraph. The calculations by the two methods disagree further in the comparison of tetraphenylethane with difluoryl, but in this case no experimental data are available.

The quantitative comparison of the calculations with experiment is much less conclusive on account of lack of accurate data. The agreement seems to be somewhat better, in general, for the HMH treatment than for the HLSP (except in the case noted in the preceding paragraph) but it is doubtful if any very great significance can really be attached to the quantitative aspects of such extremely crude calculations. (Cf. the further discussion of this point in the section entitled "Errata" at the end of this paper.)

Aliphatic as well as aryl substituents have been found to increase the dissociation of an ethane. Pauling and Wheland suggested that this effect was due to steric factors connected with the large size of the groups concerned but the explanation was not very satisfactory since it was rather inconsistent with the rest of the theory. Consequently, it is of interest to observe that by a slight extension of the HLSP method of treatment these cases can be taken care of without the necessity of introducing further hypotheses. As an illustration let us consider the molecule *n*-butane, or sym-dimethylethane. This can resonate between the unexcited structure

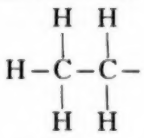


and several excited ones, such as

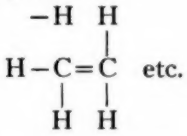


These latter, however, are very much less stable than the former since in them two single bonds have been broken in order to change a third into a double bond. Hence, such structures contribute only very slightly to the normal state of the molecule and the resonance energy is small. (It perhaps should be mentioned here that these considerations do not lead to the conclusion that the molecule should dissociate spontaneously into ethane and ethylene in the manner

indicated (except at elevated temperatures) nor are they inconsistent with the principle of the constancy of bond energies, since this type of resonance, being always present, can be considered to make a constant contribution to the energies of the bonds concerned.) The dissociated ethyl radical can also resonate in a similar way between the normal structure



and excited ones, such as



It is easily seen that the resonance is much more effective here than with the undissociated molecule since the excited structures lie relatively much lower than there. This follows from the fact that in the radical only *one* single bond must be broken to change a second into a double bond. Consequently the resonance energy of the radical is materially greater than half that of the ethane and the dissociation of the molecule is correspondingly promoted. In the case of ethane itself these considerations do not apply since resonance of the type described cannot occur. Hence we conclude that butane should be more highly dissociated than ethane or, in other words, that a methyl group is a more effective substituent than a hydrogen atom in promoting the dissociation of an ethane into free radicals. It would be rather difficult to put these purely qualitative arguments upon a satisfactory quantitative basis since the values of a number of additional integrals would be required. A rough calculation, which is not given here on account of its extreme crudity, indicates, however, that the calculated effects are probably of the correct order of magnitude to account for the observed differences between primary, secondary and tertiary alkyl groups.[19] Hückel[20] has proposed a similar explanation of these effects upon the basis of the HMH treatment.

[19] J. B. Conant, J. Chem. Phys. **1**, 427 (1933).

[20] E. Hückel, personal communication to Professor Pauling.

Electron affinity of free radicals

This problem can be easily treated by a slight extension of the HMH method. In the case of triphenylmethyl, for example, we consider the reaction

$$(C_6H_5)_3C+E^-\rightarrow(C_6H_5)_3C^-.$$

The energies of the radical and of the ion can be calculated in the usual manner. Since the secular equations are identical, the only difference between the two systems is that the latter contains one additional electron. This must be assigned to the most stable available orbit, which is seen from Hückel's calculation for the radical to have the energy q. This quantity, however, is simply the required electron-affinity and can be set equal to the experimentally determined value of -59 kcal.[21] or -2.7 e.v. This figure seems reasonable, but unfortunately cannot be checked by an independent calculation. In general, the electron-affinity of a free radical will be of the form $q+c\beta$, where c is a small constant which must be evaluated for each case individually from the secular equation. Since, however, β is also small compared with q, the second term in the expression is of minor importance and so, to a first approximation, the electron-affinity has a constant value q for all radicals. This result seems to be in satisfactory agreement with the experimental data.

It has not been found possible as yet to extend the HLSP treatment to problems of this type.

Acid strength of hydrocarbons

This problem is quite similar to the previous one, and can also be easily treated by the HMH method. Let us take triphenylmethane as an example. ΔE for the reaction

$$(C_6H_5)_3CH\rightarrow(C_6H_5)_3C^-+H^+$$

is clearly the difference between the resonance energy of the negative ion and that of the hydrocarbon, plus some additional terms connected with the energy of separating the ions, the heats of solvation, etc. If the sum of all these additional terms is called k, then we find (using the results of Hückel's calculations) $\Delta E=1.794\beta+k$. Since the value of k is completely unknown and

[21] H. E. Bent, J. Am. Chem. Soc. **52**, 1498 (1930); **53**, 1786 (1931); H. E. Bent and M. Dorfman, **54**, 1393 (1932).

since, moreover, the relation between ΔE and the dissociation constant is uncertain, this does not give a definite solution of the problem. The results of the calculation can be used for purposes of comparison, however, if two further assumptions are made; first, that k is constant for all the hydrocarbon acids under consideration and second, that the difference between the ΔE values for two compounds can be set equal to the difference between the corresponding ΔF values. Both assumptions are quite reasonable and are essentially the same as those made by Pauling and Wheland and by Hückel in their treatments of the free radicals. The ratio of the dissociation constants of two acids can now be calculated from the relation

$$\Delta E_1 - \Delta E_2 \cong \Delta F_1 - \Delta F_2 = RT \ln (K_2/K_1).$$

The results of the calculations for several hydrocarbons are given in Table III. It will be seen

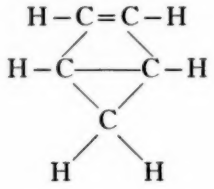
TABLE III. *Ionization of hydrocarbons.*

Hydrocarbon	ΔE	$K/K_{(C_6H_5)_3CH}$ calc.[a]	obs.[b]
Cyclopentadiene	$2.00\beta+k$	1.2×10^{3}	definitely acidic
Cycloheptatriene	$1.11\beta+k$	1.1×10^{-10}	not acidic
Phenylmethane	$0.72\beta+k$	2.0×10^{-16}	$\ll10^{-2}$
Diphenylmethane	$1.30\beta+k$	6.6×10^{-8}	$\ll10^{-1}$
Triphenylmethane	$1.79\beta+k$	1	1
Fluorene	$1.52\beta+k$	1.1×10^{-4}	$\gg2.5\times10^{4}$
Phenylfluorene	$1.98\beta+k$	5.7×10^{2}	$\gg2.5\times10^{6}$

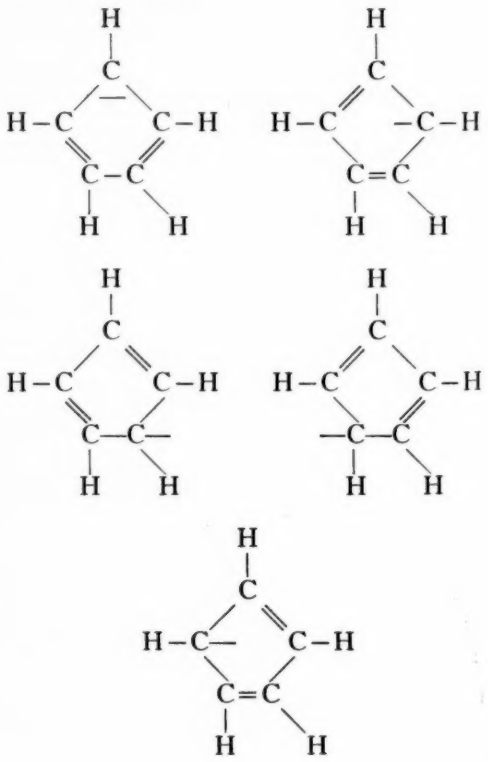
[a] Calculated for 20°C, with $\beta=-0.86$ e.v. (-19.8 kcal.).
[b] Numerical values from J. B. Conant and G. W. Wheland, J. Am. Chem. Soc. **54**, 1212 (1932).

that if fluorene and phenylfluorene are left out of account, the agreement with experiment is excellent qualitatively and perhaps satisfactory quantitatively. The error in the case of these two, however, is too large to be the result of the special assumptions used in this calculation; it must rather be attributed to the method itself. This is apparently a further case in which the neglect of the interactions between the electrons invalidates the conclusions reached by the HMH procedure.

The HLSP treatment is not so easily extended to these systems, since, in the calculations for the negative ions orbital as well as spin degeneracy has to be taken into account. This results in the introduction of several further integrals which cannot be readily evaluated. The following discussion of cyclopentadiene will illustrate the procedure that must be employed and will show the sort of results that can be obtained. The problem will be simplified by the neglect of all excited structures of the type



in which fewer than the maximum number of double bonds are formed between adjacent carbon atoms. This step is not absolutely necessary but it greatly facilitates the calculation and has the partial justification that, since the excited structures contribute more or less equally to the energies of both the hydrocarbon and the ion, their effect cancels out to some extent. With this approximation, then, the resonance energy of the hydrocarbon is seen to be zero, since only one structure is to be considered. In the ion, on the other hand, there is resonance among the five equivalent structures



The secular equation is found to be

$$\begin{vmatrix} Q-\frac{1}{2}\alpha-W & \frac{1}{2}\rho & 2\sigma & 2\sigma & \frac{1}{2}\rho \\ \frac{1}{2}\rho & Q-\frac{1}{2}\alpha-W & \frac{1}{2}\rho & 2\sigma & 2\sigma \\ 2\sigma & \frac{1}{2}\rho & Q-\frac{1}{2}\alpha-W & \frac{1}{2}\rho & 2\sigma \\ 2\sigma & 2\sigma & \frac{1}{2}\rho & Q-\frac{1}{2}\alpha-W & \frac{1}{2}\rho \\ \frac{1}{2}\rho & 2\sigma & 2\sigma & \frac{1}{2}\rho & Q-\frac{1}{2}\alpha-W \end{vmatrix} = 0,$$

where Q and α have their usual significance, ρ and σ indicate the integrals

$$\rho = (\psi_1\psi_1\psi_2\psi_3\psi_4\psi_5 | \mathrm{H} | \psi_1\psi_2\psi_2\psi_3\psi_4\psi_5)$$

and

$$\sigma = (\psi_1\psi_1\psi_2\psi_3\psi_4\psi_5 | \mathrm{H} | \psi_1\psi_2\psi_3\psi_3\psi_4\psi_5),$$

and all further integrals have been neglected. The solutions are

$$W = Q-\tfrac{1}{2}\alpha+\rho\cos 2\pi j/5+4\sigma\cos 4\pi j/5 \qquad (j=0, 1, 2, 3, 4).$$

Since ρ and σ are presumably negative, the lowest of the roots is that with $j=0$ and the resonance energy becomes $\rho+4\sigma$. ΔE of ionization is thus $\rho+4\sigma+k$. By the same procedure, ΔE of ionization for cycloheptatriene is found to be $0.455\rho+2.492\sigma+k$ and accordingly the calculation agrees with experiment in predicting that cyclopentadiene should be the stronger acid. Unfortunately, it has not been found possible to extend this treatment to more complicated systems of this type.

Basicity of aryl carbinols

The basic strength of triphenylcarbinol and similar compounds can be treated in a manner completely analogous to the above. Since, however, suitable experimental data are not available for purposes of comparison, we shall not go into the problem here.

Conclusion

Two methods have been described for the quantum-mechanical treatment of unsaturated and aromatic organic molecules. In general these lead to very similar results but occasionally definite discrepancies do occur. In such cases, a comparison with experiment shows that the HLSP treatment is somewhat more reliable than the HMH, a result which can be anticipated on the basis of the greater rigor of the former. The HMH procedure, on the other hand, has shown itself superior to the HLSP in its ability to treat a wider variety of problems (although not always successfully, as, for example, the acid strengths of fluorene and phenylfluorene). This is a consequence of its simpler mathematical form. In general it would seem wise to carry through the calculation by both methods wherever possible and to check each against the other.

I wish to thank Professor Linus Pauling for his valuable help and criticism in the preparation of this paper, and Dr. Jack Sherman for his assistance in checking many of the calculations.

Errata

The Nature of the Chemical Bond. V

LINUS PAULING AND G. W. WHELAND, *California Institute of Technology, Pasadena*

(J. Chem. Phys. **1**, 362, 1933)

In this paper a number of numerical errors appeared. The corrected values are given below.

Substitute the following for the corresponding lines in Table III, p. 370:

Radical	W'	W	$W-W'$
Biphenylmethyl	$Q+3.8000\alpha$	$Q+4.4473\alpha$	0.6473α
Phenylfluoryl	$Q+5.2000\alpha$	$Q+6.2764\alpha$	1.0764α
Biphenyldiphenylmethyl	$Q+7.6000\alpha$	$Q+8.7738\alpha$	1.1738α
Phenyldibiphenylmethyl	$Q+9.5000\alpha$	$Q+10.7347\alpha$	1.2347α
Tribiphenylmethyl	$Q+11.4000\alpha$	$Q+12.6905\alpha$	1.2905α

And in Table IV, p. 371:

Radical	Position of odd electron	Number of structures	Relative values of coefficients
Biphenylmethyl	methyl carbon	4	1
	biphenyl group	9	0.5608
Biphenyldiphenylmethyl	methyl carbon	16	1
	phenyl group	48	0.8861
	biphenyl group	36	0.7816
Phenyldibiphenylmethyl	methyl carbon	32	1
	phenyl group	48	0.8433
	biphenyl group	144	0.7392
Tribiphenylmethyl	methyl carbon	64	1
	biphenyl group	432	0.7007

The discussion in section (*c*), page 373, regarding the quantitative agreement of the calculations with experiment has to be altered somewhat in accordance with the corrected values of the free radical resonance energies. The calculated dissociation constant of hexabiphenylethane now becomes $(3.0)^{18}\times 4.1\times 10^{-4}=1.6\times 10^{5}$. This value is in good agreement with the reported complete dissociation of the molecule, but may be too high. In general, the constants found in this manner for the various hexaarylethanes seem to be uniformly too large, in comparison with that of hexaphenylethane. This discrepancy may perhaps arise from the neglect of excited structures or may be due to the fact that we are comparing small differences between larger quantities. A third possibility is that the value of α assumed in the calculations is too large (in absolute magnitude). This would be in accordance with the views of Penney.[22] It is significant, however, that the qualitative agreement with experiment is now perfect, the empirical order given on page 368 being reproduced without error.

[22] W. G. Penney, Proc. Roy. Soc. **A144**, 166 (1934).

A Calculation of the Equilibria in Keto-Enol Tautomerism

G. W. WHELAND, *California Institute of Technology, Pasadena*

(J. Chem. Phys. **1**, 731, 1933)

Delete the diagonal bonds extending from *R* to the carbonyl carbon atom in structures XII-XVI inclusive (page 733).

Quantum Theory of the Latent Photographic Image

T. Howard James and J. J. Coleman, *University of Colorado, Boulder, Colorado*

(Received March 22, 1934)

A general formulation involving quantum ideas is given for the relation between the amount of photolytic action in latent image formation and the amount of light producing it. A method of deducing the number of "effective" quanta per grain necessary to produce developability is given. Slow process emulsions require, in general, the absorption of from 3 to 4 "effective" quanta. This number agrees with that found for physical development by Reinders and Hamburger. Faster emulsions require a smaller number (1 to 2), showing presumably the presence of more highly developed sensitivity centers. The number for any emulsion should depend to some extent upon the developer used. Parametric equations are given which relate the amount of photolytic product to the number of developable grains. These equations lead to a characteristic curve which has a point of inflection when the number of "effective" quanta required per grain is greater than one but none when the number is equal to one.

I

IT has been proposed[1] that during the period of light-action upon a photographic emulsion, the building up of a developable density is accompanied by a reverse reaction. It was suggested[2] that this conception must be incorporated with a quantum theory of latent image formation in order to obtain a satisfactory relation between the net amount of photolytic action and the amount of light producing it. On this basis, a modified form of Elder's equation was derived.

In the original formulation of the theory[2] the true state of affairs was approximated by assuming that the absorption of one quantum by a sensitized area, i.e., a more or less restricted area containing a pro-nucleus, rendered a grain developable and that in considering the effect of the reverse reaction we could ignore the grains in which that area had absorbed more than one quantum. The theory was further marred by the use of the notion of a "time lag." It is the purpose of this paper to develop the theory in a more rigorous fashion and to consider some of the consequences of this formulation. The assumption that one quantum alone suffices to produce a developable grain is valid only in special cases. In general, however, the assumption is untenable[3] and a method will be given for determining (approximately) the number of *effective* quanta required to produce a developable center on a grain. However, the gain in elegance and precision is somewhat at the expense of serviceableness, for we cannot apply the modified theory to density measurements unless we are dealing with emulsions with a uniform grain size and we have given the "maximum ideal developable density" (i.e., the density which would be produced if all of the grains were developable).

Fundamentally, the theory is of great simplicity. We assume: (1) When a quantum of sufficient energy is absorbed by a given grain, one ion or perhaps a group of ions are modified in such a way that, when a sufficient number of modifications are produced within a more or less restricted area, a development center results and the grain as a whole becomes developable by the developer concerned. We shall for convenience term the product of one absorbed quantum in an "effective" area of grain an "active center," emphasizing that one of them alone does not, in general, constitute a development center. The "effective" area refers to that

[1] Svedberg and Anderson, Phot. J. **48**, 272 (1924); Lüppo-Cramer, *Proceedings of the 7th Int. Cong. Phot.*, p. 45 (1928) (General references are given.); Kieser, Zeits. f. wiss. Phot. **26**, 275 (1929); Sheppard, Ind. Eng. Chem. **22**, 555 (1930); Blair and Leighton, J. Phys. Chem. **36**, 1649 (1932).

[2] James, J. Chem. Phys. **2**, 132 (1934).

[3] Cf. Sheppard, Trivelli and Loveland, J. Frank. Inst. **200**, 51 (1925); Reinders and Hamburger, Zeits. f. wiss. Phot. **31**, 265 (1933).

region from which the "active center" may act with a pro-nucleus, by itself or with other similar centers within the region, or with other centers alone, to produce a development center. (2) These centers have a tendency to change either spontaneously or under the influence of various agents (light quanta, chemicals, etc.) to a non-active state which cannot contribute to developability of the grain. (3) If β is the number of ions (or groups of ions) which are available in N grains for the production of active centers and s the number of active centers present at any time, then the speed of the "forward reaction" is proportional to $(\beta-s)$. (4) The speed of the "reverse reaction" is proportional to s itself.

The equation for the rate of formation of the active centers is then

$$ds/dt=K_1(\beta-s)-K_2s \tag{1}$$

in which K_1 and K_2 depend upon the intensity and wave-length of the incident light, the nature of the emulsion and other factors. The equation yields upon integration and evaluation of the constants of integration (we take $t=0$ when $s=0$)

$$s=s_m(1-e^{-Kt}) \tag{2}$$

or

$$\ln\,(1-s/s_m)=-Kt \tag{2a}$$

in which

$$s_m=\beta/(1+K_2/K_1), \tag{3}$$

$$K=K_1+K_2. \tag{4}$$

By Eq. (2) it is evident that s_m is the maximum number of centers producible by light of a given wave-length and intensity, i.e., the number present at equilibrium.

There is at present no way of counting the active centers and therefore Eq. (2) cannot be tested directly. The value of s must be determined either from counts of the number of developable grains or from density measurements. As we have already stated, density data can only be used with uniform grain emulsions and when the value of the maximum ideal developable density, b, is known. This information is, unfortunately, lacking in the majority of the published data. If we know b, then since the density is proportional to the number of developable grains, we shall have

$$k/N=D/b \tag{5}$$

in which k is the number of developable grains, N the total number of grains and D the density. The ratio s/s_m, required by Eq. (2a), can be calculated from k/N as follows:

Silberstein[4] has presented an equation which expresses s/N in terms of k/N[5] and since we can put

$$s/s_m=(s/N)/(s_m/N)=(s/N)/(s/N)_m \tag{6}$$

in which $(s/N)_m$ is the maximum value of s/N, we can thus obtain the ratio s/s_m. Silberstein's equation is

$$k/N=1-e^{-s/N}\sum_{i=0}^{r-1}\frac{1}{i!}(s/N)^i, \tag{7}$$

where r is the number of active centers necessary to produce a developable grain. A derivation of this equation will be given in the next section. Eq. (2a) shows that a straight line should be obtained by plotting $\ln\,(1-s/s_m)$ against t. Hence such plots made for various values of r, if a straight line can be obtained, both confirm the validity of Eq. (2a) and give us the correct value of r. Such straight lines were obtained in all of the sets of data tried. In Figs. 1 and 2 we give two illustrations.

The data used to obtain Fig. 1 are by Toy (Table 5, reference 2). The graph in this case very definitely indicates 3 as the proper value of r. Fig. 2 (data by Trivelli and Loveland, Table 4, reference 2) does not yield as pronounced a divergence from a straight line for values of r adjacent to the correct value but the divergence is definitely present, in this case for small values of exposure.[6] The results obtained for other sets of data are given in Table I. In some cases the graphs allow no choice between two consecutive values of r but definitely exclude all others.

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[4] Silberstein, Phil. Mag. **5**, 464 (1928).

[5] Silberstein's formula expresses ϵan, the average effective number of quanta in each grain, assuming all to have equal area a, in terms of k/N. By the above definition, $s=\epsilon anN$, and hence $\epsilon an=s/N$. We are not, in this paper, considering the effect of the size of the grains and formula (7) is not restricted to emulsions with uniform grain size (see derivation, section II).

[6] The value of x_m where $x=k/N$ for this emulsion was redetermined by careful extrapolation to be 0.64. The old value, 0.65, yields however the same value of r.

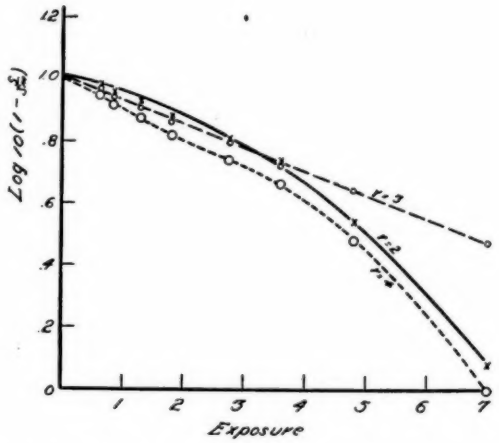

FIG. 1. Graph of log $10(1-s/s_m)$ against exposure, E.

Strictly speaking, Eq. (7) is valid only for cases in which the number of active centers required for developability is the same for all of the grains in the emulsion. However, at least a small fraction of the grains undoubtedly require a number of centers different from that found for the plate as a whole.

It is to be expected that the value of r will depend upon the emulsion and to some extent upon the developer used. The theory of Sheppard, Trivelli and Loveland[7] that the number of quanta required to render a grain developable depends upon the size of the "pro-nuclei" present in the grain before exposure, is of interest in this connection. Reference to Table I

TABLE I. *Values of r for various emulsions.*

Emulsion	Grain size	s_m/N	r	Investigator
Ilford Process	$0.3\mu^2$	8.5	3	Toy, Phil. Mag. **45**, 719 (1923)
Special. Uniform grain size	—	6.3	3	Toy, Phot. J. **61**, 420 (1921)
Eastman 40	$0.4\mu^2$	2.0	2	Trivelli and Loveland, quoted by Silberstein, Phil. Mag. **45**, 483 (1923)
Eastman Slow Process	$0.115\mu^2$	7.8–9.2	4–5	Trivelli and Loveland, from Fig. 1. Silberstein, Phil. Mag. **5**, 464 (1928)
	$0.7\mu^2$	10–10.6	3–4	
High speed	$0.98\mu^2$	2.6–5.5	1–3*	Toy, Phil. Mag. **44**, 365 (1922)
	$1.75\mu^2$	3.3	1	
	$2.75\mu^2$	3.75	1	
Special Eastman Lantern slides**	—	3.0–4.8	1–2	Lester, quoted by James, J. Chem. Phys. **2**, 135 (1934)

* Correct value uncertain, probably 2.

** Exposure by x-rays.

[7] Sheppard, Trivelli and Loveland, J. Frank. Inst. **200**, 51 (1925).

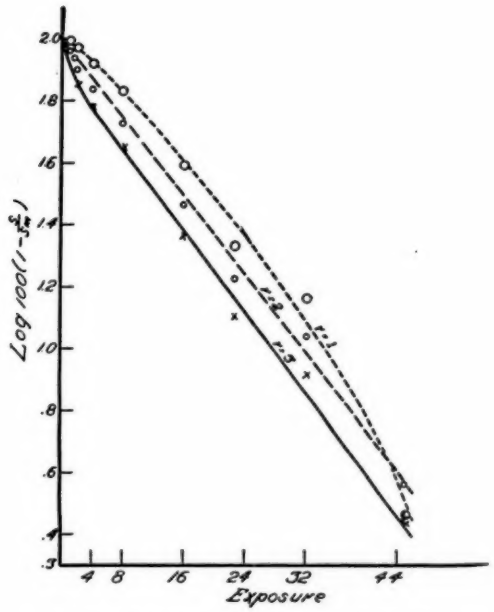

FIG. 2. Graph of log $100(1-s/s_m)$ against exposure, E.

will show that in one set of data by Toy the value of r is one. This emulsion would be, on this theory, one which was approaching the limit beyond which an emulsion cannot be ripened without fog. We should expect that, grain size being constant, the sensitivity of various emulsions would depend both upon their power to absorb light and upon the value of r. Unfortunately no usable data are available with which to test this hypothesis. It is further to be noted that in Toy's data we have three different grain sizes. The differences in sensitivity exhibited by these sets may well be ascribed to differences in the sizes of the grains.

It is interesting to note that the density-exposure data for α-particles fit well within the experimental error the simple equation of reference (2)[8] without a "time lag," i.e., the equation

$$x = x_m(1-e^{-Kt}). \tag{8}$$

This relation also holds approximately for x-rays[9] indicating in each case that r is probably one. This is, perhaps, to be expected in view of

[8] Svedberg and Andersson, Phot. J. **61**, 325 (1921).

[9] Svedberg, Phot. J. **62**, 310 (1922).
Trivelli, *VIII Int. Cong. Phot.*, p. 378 (1931).

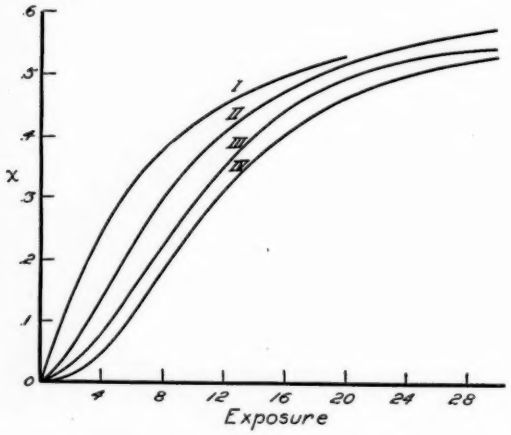

FIG. 3. Characteristic curves determined from the parametric Eqs. (2) and (7).

the large energy of x-ray quanta and of α-particles.

In the foregoing development no definite assumptions were made as to the nature of the active centers. The theory is, insofar as the development of the quantitative formulation is concerned, independent of such assumptions as long as the four fundamental postulates enumerated above remain valid. It is nevertheless desirable to show the application of this formulation to modern theory of the mechanism of latent image formation.

The evidence at present points strongly to the following mechanism for the primary action of an absorbed quantum:

$$Br^- + h\nu = Br + \epsilon.$$

This ". . . photo-ionization process is essentially virtual. If the electrons are not taken over by silver ions, the halogen atoms by some acceptor, the process must reverse."[10] If the electron is taken over by a silver ion, a silver atom results, which is the manifestation of an "active center."

If this mechanism is correct, then the process of developable center formation is similar to that with which Reinders and Hamburger[11] were concerned in their studies of physical development. It is interesting to note that the value of r is from 3 to 4 for most slow emulsions and that this agrees with the results of Reinders and Hamburger (most probable value, 4).

It is not necessary to assume that the value of r represents the total number of atoms which are produced in the entire grain. It is rather the number produced in the "sensitive" area (used in the sense already indicated rather than referring to any sensitizing action of dyes) of the grain. Only quanta absorbed in this area are *effective* quanta. This area may represent the effective area around a sensitivity speck in the grain; i.e., that area from which the silver atoms could concentrate upon the sensitivity speck and thus tend to produce a developable center. It is conceivable that this area is dependent upon temperature to some extent. Moreover, Silberstein's work indicates that no great error would arise in the calculations if there exist several such areas upon each grain, as will, indeed, usually be the case.

Fig. 3 gives four "characteristic curves" calculated from the parametric Eqs. (2) and (7). The values of r range from 1 to 4, and those of x_m are approximately 0.6. It will be seen that these curves represent adequately the general form of the experimental characteristic curve. The presence or absence of a point of inflection is governed by the value of r and hence is dependent upon the nature of the emulsion. The "time lag" previously assumed to exist in certain cases[2] appears quite naturally and not as something foreign to the theory.

II

Consider a state of exposure which is the result of exactly s quanta, i.e., s quanta have been effective in producing "active centers." Any of the quanta can act upon any of the N different grains and accordingly all of the quanta can act upon all of the grains in N^s different ways.

If, now, it be required that a particular grain be unaffected, the number of possible ways in which the quanta can act upon the remaining grains is $(N-1)^s$. If it be required that this particular grain be affected by one and only one quantum, this condition can be satisfied in exactly the number of ways in which one quantum can be chosen out of a total of s;

[10] Sheppard, Ind. Eng. Chem. **22**, 555 (1930) (Nichols Medal Lecture).

[11] Reinders and Hamburger, Zeits. f. wiss. Phot. **31**, 32 (1932) and **31**, 265 (1933).

namely, in s different ways. In each case there will be $(N-1)^{s-1}$ ways in which the remaining quanta can act upon the remaining grains. Hence, the total number of ways in which the grains can be exposed under the condition that some particular grain be affected by exactly one quantum is $s(N-1)^{s-1}$. In general, the number of ways of exposing the grains under the condition that a particular grain be acted upon by exactly i quanta is,

$$[s!/(i!(s-i)!)](N-1)^{s-i}$$

in which $s!/i!(s-i)!$ is the number of ways of selecting i quanta out of a total of s.

If all of the ways of making the grains developable are equally probable, then the probability that exactly i quanta out of a total of s effective quanta will act upon a particular grain in a given exposure is given by

$$\frac{s!}{i!(s-i)!}\frac{(N-1)^{s-i}}{N^s}=\frac{s!}{i!(s-i)!}\frac{1}{(N-1)^i}\left(\frac{N-1}{N}\right)^s.$$

If P is the probability that a given grain be affected by *at least* r quanta, then

$$P=\sum_{i=r}^{s}\frac{s!}{i!(s-i)!}\frac{1}{(N-1)^i}\left(\frac{N-1}{N}\right)^s$$

$$=\left(\frac{N-1}{N}\right)^s\left[\sum_{i=0}^{s}\frac{s!}{i!(s-i)!}\left(\frac{1}{N-1}\right)^i-\sum_{i=0}^{r-1}\frac{s!}{i!(s-i)!}\left(\frac{1}{N-1}\right)^i\right].$$

The first summation is merely the binomial expansion of

$$(1+1/(N-1))^s=(N/(N-1))^s,$$

therefore

$$P=1-\left(\frac{N-1}{N}\right)^s\sum_{i=0}^{r-1}\frac{s!}{i!(s-1)!}\left(\frac{1}{N-1}\right)^i.$$

Since both N and s are very large, the fraction of the total number of grains which are acted upon by at least r quanta (where $r\ll s$ and $r\ll N$) will be (approximately) the same in all of a number of exposures of identical plates. Moreover this fraction will be the probability that a particular grain in a given exposure be acted upon by at least r quanta. Hence if k is the number of grains that have been acted upon by *at least r effective* quanta, then

$$\frac{k}{N}=P=1-\left(\frac{N-1}{N}\right)^s\times\sum_{i=0}^{r-1}\frac{s!}{i!(s-i)!}\left(\frac{1}{N-1}\right)^i \quad \begin{matrix} r\ll s \\ r\ll N. \end{matrix} \tag{9}$$

This equation is exact but a more convenient approximation will be of sufficient accuracy for the present purposes. We can put

$$((N-1)/N)^s=(1-1/N)^{N(s/N)}=e^{-s/N},$$

since $(1-1/N)^N$ is asymptotically equal to e^{-1} for large N. Furthermore

$$s!/(s-i)!=s(s-1)(s-2)\cdots(s-i+1)$$

and since $r\ll s$, and hence $i\ll s$ in each term of the summation in (9),

$$s!/(s-1)!=s^i$$

approximately. Finally, 1 can be neglected in comparison to N in the factors $[1/(N-1)]^i$ as long as i is small. (Note that these last two approximations tend to cancel each other.) Eq. (9) can now be written:

$$k/N=x=1-e^{-s/N}\sum_{i=0}^{r-1}\frac{1}{i!}(s/N)^i. \quad \begin{matrix} r\ll N \\ r\ll s \end{matrix} \tag{10}$$

This is the equation first presented by Silberstein.[4]

Wave-Mechanical Treatment of the Naphthalene Molecule

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(Received June 14, 1934)

The secular equation corresponding to the forty-two canonical structures for naphthalene has been set up and solved rigorously (except for the neglect of certain exchange integrals), the energy value obtained being 2.0400α greater than that corresponding to one of the unexcited structures, in which α is the single exchange integral between adjacent carbon atoms. The equation has also been solved by various simplified procedures, and it has been found that the assumptions made in the earlier treatment of Pauling and Wheland are to a considerable extent justified. The coefficients of the various structures in the wave function for the normal state have been evaluated. It has been found that of the three unexcited structures the symmetrical one makes approximately a 50 percent greater contribution to the wave function than either of the two unsymmetrical structures. Some further discussion of the magnitudes of the coefficients is given.

INTRODUCTION

A quantum-mechanical discussion of aromatic molecules has recently been given by Pauling and his co-workers.[1] The resonance energies of a number of molecules were obtained by setting up and solving the secular equations corresponding to the canonical structures for these molecules. The matrix elements in the secular matrix were calculated by the graphical method developed by Pauling.[2] Since the number of linearly independent structures increases very rapidly with increase in the size of the system, the secular equation is usually of very high degree. Thus for naphthalene the secular equation is of the forty-second degree and for anthracene it is of the four hundred twenty-ninth degree. In solving these equations, certain simplifying assumptions were made so as to reduce them to equations of low degree, the main assumption being suggested by chemical considerations; namely, that all first-excited structures (which contain one less than the maximum number of double bonds) could be given the same coefficient in the wave function for the normal state, and similarly for second-excited structures (which contain two less than the maximum number of double bonds), etc. In addition it was assumed that for very complicated molecules the second- and higher-excited structures could be neglected entirely without introducing any appreciable error in the value of the energy.

It is the purpose of this paper to give a thorough treatment of the naphthalene molecule and to discuss the errors in the energy value and the wave function caused by these assumptions. It has been found that the earlier approximations are to a great extent justified.

THE SECULAR EQUATION FOR NAPHTHALENE

The secular equation for naphthalene is set up in the same manner as was done by Pauling and Wheland.[1] Each carbon atom is considered to possess two K electrons and four L electrons, one for each of the four orbital functions formed by a linear combination of one $2s$ and three $2p$ orbitals. Three of the L orbitals form single bonds to the attached hydrogen atom and the two adjacent carbon atoms. The fourth orbital for each atom is a pure p orbital projecting at right angles to the plane of the ring. Only the interactions of the electrons in these orbitals are considered and one electron is assigned to each orbital; i.e., naphthalene is treated as a ten-electron system with spin degeneracy only. Furthermore, all exchange integrals of unity and all exchange integrals of the energy except single exchange integrals between two adjacent atoms are neglected. These single exchange integrals

[1] L. Pauling and G. W. Wheland, J. Chem. Phys. **1**, 362 (1933).
L. Pauling and J. Sherman, J. Chem. Phys. **1**, 606, 679 (1933).

[2] L. Pauling, J. Chem. Phys. **1**, 280 (1933).

are all assumed to have the same value (although this is not required by the symmetry of the naphthalene molecule) and are denoted by the symbol α. The Coulomb integral is denoted by Q and the energy by W. The number of canonical (linearly independent) structures is forty-two, so that the secular equation is of the forty-second degree. This can be factored into a sixteenth, a fourteenth, and two sixth-degree factors by considering the symmetry of the molecule. The presence of the two planes of symmetry perpendicular to the plane of the ring makes it possible to form linear combinations of the forty-two structures which are symmetric-symmetric, antisymmetric-antisymmetric, symmetric-antisymmetric, or antisymmetric-symmetric with respect to these two planes. The symmetric-symmetric combination, formed by giving all structures in a set related by these planes of symmetry the same coefficient, gives rise to the sixteenth-degree factor, and this alone need be considered in evaluating the energy of the normal state. The matrix elements of this sixteenth-degree equation, each divided by α, are given in Table I, the symbol x signifying $(Q-W)/\alpha$. The corresponding sets of structures are given in Fig. 1.

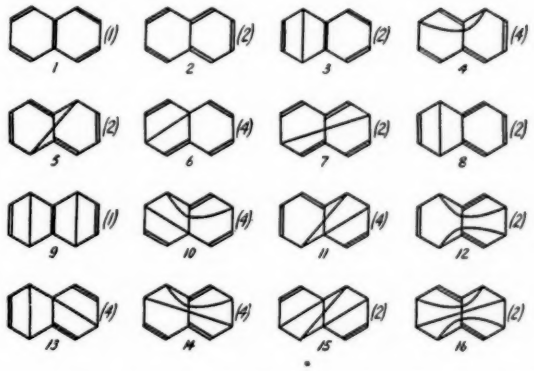

FIG. 1. Sets of canonical structures corresponding to the secular matrix given in Table I. The number in parenthesis following each structure denotes the number of structures in the set. The remaining structures are obtained from the given one by reflection through the two planes of symmetry perpendicular to the plane of the ring.

SOLUTION OF THE SECULAR EQUATION

Method

The secular equation has been solved under the following procedures:

TABLE I. *Matrix elements in the secular equation for naphthalene.*

	1	2	3	4	5	6	7	8
1	$x+2$	$x/2+13/4$	$x+7/2$	$x/2+4$	$x/8+11/8$	$2x+7$	$x/2+5/2$	$x/4+2$
2	$x/2+13/4$	$17x/8+43/8$	$5x/4+11/2$	$5x/2+41/4$	$x+5$	$5x/2+11$	$x+5$	$5x/4+11/2$
3	$x+7/2$	$5x/4+11/2$	$5x/2+7/2$	$5x/4+31/4$	$x/2+4$	$2x+23/2$	$x/2+4$	$x+5$
4	$x/2+4$	$5x/2+41/4$	$5x/4+31/4$	$25x/4+53/4$	$5x/2+8$	$13x/4+65/4$	$5x/2+29/4$	$2x+17/2$
5	$x/8+11/8$	$x+5$	$x/2+4$	$5x/2+8$	$5x/2+7/2$	$x+13/2$	$5x/8+25/8$	$2x+4$
6	$2x+7$	$5x/2+11$	$2x+23/2$	$13x/4+65/4$	$x+13/2$	$7x+37/2$	$5x/2+8$	$5x/4+31/4$
7	$x/2+5/2$	$x+5$	$x/2+4$	$5x/2+29/4$	$5x/8+25/8$	$5x/2+8$	$17x/8+19/8$	$x/2+13/4$
8	$x/4+2$	$5x/4+11/2$	$x+5$	$2x+17/2$	$2x+4$	$5x/4+31/4$	$x/2+13/4$	$5x/2+7/2$
9	$x/4+5/4$	$x/2+5/2$	$x+2$	$x/2+4$	$x/2+5/2$	$x/2+4$	$x/8+11/8$	$x+2$
10	$x+5$	$2x+17/2$	$x+8$	$7x/2+29/2$	$5x/4+25/4$	$5x+13$	$2x+7$	$x+13/2$
11	$x/2+4$	$5x/2+29/4$	$5x/4+31/4$	$13x/4+65/4$	$5x/2+8$	$13x/4+53/4$	$x+29/4$	$2x+17/2$
12	$x/8+11/8$	$x+17/4$	$x/2+13/4$	$5x/2+29/4$	$x+7/2$	$x+13/2$	$x+7/2$	$5x/4+5/2$
13	$x+5$	$2x+10$	$5x/2+8$	$7x/2+23/2$	$2x+7$	$7x/2+16$	$5x/4+25/4$	$5x/2+8$
14	$x/2+4$	$5x/2+29/4$	$5x/4+25/4$	$4x+31/2$	$x+13/2$	$13x/4+59/4$	$5x/2+29/4$	$5x/4+25/4$
15	$x/2+5/2$	$x+7/2$	$x/2+4$	$x+29/4$	$5x/8+25/8$	$5x/2+5$	$5x/8+31/8$	$x/2+13/4$
16	$x/8+11/8$	$x+7/2$	$x/2+5/2$	$5x/2+17/4$	$5x/8+25/8$	$x+13/2$	$x+7/2$	$x/2+13/4$

	9	10	11	12	13	14	15	16
1	$x/4+5/4$	$x+5$	$x/2+4$	$x/8+11/8$	$x+5$	$x/2+4$	$x/2+5/2$	$x/8+11/8$
2	$x/2+5/2$	$2x+17/2$	$5x/2+29/4$	$x+17/4$	$2x+10$	$5x/2+29/4$	$x+7/2$	$x+7/2$
3	$x+2$	$x+8$	$5x/4+31/4$	$x/2+13/4$	$5x/2+8$	$5x/4+25/4$	$x/2+4$	$x/2+5/2$
4	$x/2+4$	$7x/2+29/2$	$13x/4+65/4$	$5x/2+29/4$	$7x/2+23/2$	$4x+31/2$	$x+29/4$	$5x/2+17/4$
5	$x/2+5/2$	$5x/4+25/4$	$5x/2+8$	$x+7/2$	$2x+7$	$x+13/2$	$5x/8+25/8$	$5x/8+25/8$
6	$x/2+4$	$5x+13$	$13x/4+53/4$	$x+13/2$	$7x/2+16$	$13x/4+59/4$	$5x/2+5$	$x+13/2$
7	$x/8+11/8$	$2x+7$	$x+29/4$	$x+7/2$	$5x/4+25/4$	$5x/2+29/4$	$5x/8+31/8$	$x+7/2$
8	$x+2$	$x+13/2$	$2x+17/2$	$5x/4+5/2$	$5x/2+8$	$5x/4+25/4$	$x/2+13/4$	$x/2+13/4$
9	$x-1$	$x/4+11/4$	$x/2+4$	$x/2+1$	$x+5$	$x/2+5/2$	$x/8+11/8$	$x/8+11/8$
10	$x/4+11/4$	$11x/2+13/2$	$7x/2+10$	$5x/4+25/4$	$5x/2+25/2$	$7x/2+23/2$	$2x+4$	$5x/4+25/4$
11	$x/2+4$	$7x/2+10$	$25x/4+17/4$	$x+29/4$	$7x/2+23/2$	$5x/2+11$	$5x/2+11/4$	$x+23/4$
12	$x/2+1$	$5x/4+25/4$	$x+29/4$	$17x/8-5/8$	$5x/4+25/4$	$5x/2+17/4$	$x/4+11/4$	$x+7/2$
13	$x+5$	$5x/2+25/2$	$7x/2+23/2$	$5x/4+25/4$	$11x/2+13/2$	$2x+13$	$5x/4+25/4$	$5x/4+13/4$
14	$x/2+5/2$	$7x/2+23/2$	$5x/2+11$	$5x/2+17/4$	$2x+13$	$25x/4+23/4$	$x+23/4$	$5x/2+17/4$
15	$x/8+11/8$	$2x+4$	$5x/2+11/4$	$x/4+11/4$	$5x/4+25/4$	$x+23/4$	$17x/8-29/8$	$x/4+11/4$
16	$x/8+11/8$	$5x/4+25/4$	$x+23/4$	$x+7/2$	$5x/4+13/4$	$5x/2+17/4$	$x/4+11/4$	$17x/8-29/8$

I. All structures are taken into account in the following ways:

a. The sixteenth-degree equation is solved rigorously by the method described by James and Coolidge.[3] The procedure consists in substituting two approximate values of the root into the determinant and then evaluating the determinant. A linear interpolation or extrapolation of these two values is then made in order to obtain a better approximation to the root.

b. All first-excited structures are grouped together by giving them the same coefficient, and similarly for the second and third-excited structures. The resultant equation is of the fifth degree.

II. The third-excited structures only are neglected. The remaining structures are then grouped together as in the previous treatment. The resultant equation is of the fourth degree.

III. Only the unexcited and first-excited structures are considered. The following procedures are carried out:

a. The resultant eighth-degree equation is solved rigorously.

b. All first-excited structures are grouped together by giving them the same coefficient. The resultant equation is of the third degree.

c. The individual sets of first-excited structures are first normalized and then grouped together to give a resultant equation of the third degree.

IV. The quadratic equation involving only the three unexcited structures is solved.

Results

The results obtained under the various procedures for solving the secular equation are summarized in Table II. It is seen that resonance among the three unexcited structures alone yields 1.3703α for the value of the resonance energy (procedure IV); this is only 67 percent of the total resonance energy. If the first-excited structures are now included, the resonance energy is increased to 2.0036α (procedure IIIa), each of the sixteen structures making an average contribution of 0.0396α as compared to the average contribution of each unexcited structure of 0.457α. This value of 2.0036α is only 2 percent less than the value 2.0400α obtained in the complete treatment. If the eighth-degree equation involving these structures is reduced to a cubic by grouping together the first-excited structures (procedure IIIb), it is seen that the resultant energy value is only 0.0276α less than that obtained by solving the eighth-degree equation rigorously. If the second-excited structures are now included, the resonance energy is increased to 2.0172α (procedure II), each of the nineteen second-excited structures making an average contribution of only 0.0022α. If all the structures are considered, it is seen that the energy value resulting from the approximate treatment (procedure Ib) is 2.0175α, only 1 percent less than that obtained by solving the sixteenth-degree equation rigorously. The four third-excited structures make only a very small contribution, the average value per structure being only 0.00008α.

Conclusions

The above results indicate that the best approximate solution of the secular equation is obtained when all of the canonical structures are taken into account by grouping together all first-excited structures, all second-excited structures, etc., as was done by Pauling and Wheland. This procedure seems reasonable from chemical

TABLE II. *Resonance energy of naphthalene.*

	Total energy	Resonance energy
Single unexcited structure	$Q+2\alpha$	0
I. All structures are considered		
a. rigorous solution of the complete equation	$Q+4.0400\alpha$	2.0400α
b. all first-excited structures are assumed to have the same coefficient and similarly for higher-excited structures	$Q+4.0175\alpha$*	2.0175α*
II. Third-excited structures are neglected. Remaining structures are grouped as in Ib.	$Q+4.0172\alpha$	2.0172α
III. Only unexcited and first-excited structures are considered		
a. rigorous solution of eighth degree equation	$Q+4.0036\alpha$	2.0036α
b. all first-excited structures are assumed to have the same coefficient	$Q+3.9760\alpha$	1.9760α
c. each set of first-excited structures is normalized and then all are grouped together	$Q+3.9682\alpha$	1.9682α
IV. Only the unexcited structures are considered	$Q+3.3703\alpha$	1.3703α

* These values differ from those given by Pauling and Wheland (reference 1) because of an error in one of the matrix elements of their equation, and also because they solved the fifth-degree equation only approximately. In the secular equation given on page 366, the 3,4 and 4,3 matrix elements should be corrected to read $(531/8)(Q-W)+2175\alpha/8$.

[3] H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933).

considerations, inasmuch as all first-excited structures have one less than the maximum number of double bonds and may therefore be expected to contribute about equally to the energy of the normal state. In naphthalene the error introduced in the energy value by this procedure is only 1 percent of the resonance energy. It may be expected to increase slowly with the size of the molecule.

Although the error introduced by neglecting all second and higher-excited structures in naphthalene is only 2 or 3 percent, this error may be expected to increase fairly rapidly as we go to more complicated molecules, inasmuch as the number of these higher-excited structures increases very rapidly relative to the increase in the number of first-excited structures. Thus, in anthracene the total number of canonical structures (429) is slightly more than ten times the number of naphthalene (42). However, the number of first-excited structures increases only three-fold (48/16) whereas the total number of higher-excited structures increases more than sixteen-fold (377/23).

The Wave Function for the Normal State

Having solved the secular equation for the energy of the normal state, the coefficients of the structures in the wave function can then be evaluated in the usual manner. The results (before normalizing) obtained under the various assumptions used in solving the secular equation are tabulated in Table III. It is seen that when all the structures are taken into account, as in procedure Ib, the coefficients approximate the values obtained in the complete treatment rather closely, and, moreover, neglect of the third-excited structures (II) produces only a small change. On the other hand the rougher approximations lead to large errors even in the relative values of the coefficients for the unexcited structures.

TABLE III. *Relative values of the coefficients of the canonical structures of naphthalene in the wave function for the normal state.*

Structures in set	Coefficients under assumption Ia	Ib	II	IIIa	IIIb	IIIc	IV
1	1	1	1	1	1	1	1
2	0.654	0.618	0.623	0.993	0.851	0.854	0.876
3	.453	.228	.229	.744	.303	.521	0
4	.283	.228	.229	.428	.303	.521	0
5	.259	.228	.229	.352	.303	.521	0
6	.245	.228	.229	.588	.303	.521	0
7	.238	.228	.229	.237	.303	.521	0
8	.218	.228	.229	.451	.303	.521	0
9	.206	.084	.085	0	0	0	0
10	.114	.084	.085	0	0	0	0
11	.106	.084	.085	0	0	0	0
12	.076	.084	.085	0	0	0	0
13	.069	.084	.085	0	0	0	0
14	.046	.084	.085	0	0	0	0
15	.055	.016	0	0	0	0	0
16	.011	.016	0	0	0	0	0

It is striking that of the three unexcited structures, the symmetrical one makes a 50 percent greater contribution to the wave function than either of the two unsymmetrical structures, the relative values of the coefficients in the complete treatment being 1 to 0.654. It is also to be noticed that the coefficient of the symmetrical second-excited structure labelled 9 is nearly twice as great as the next largest coefficient for a second-excited structure and is only slightly less than the smallest coefficient of the first-excited structures. The coefficient of the third-excited structures in set 15 is seen to be greater than that for the second-excited structures in set 14.

The above results indicate that the procedure which yields the most nearly correct value of the energy also yields the best approximation to the values of the coefficients.

The Theory of the Structure of Hydrogen Peroxide and Hydrazine

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The method of electron pairs has been applied to determine the most stable configuration for the atoms in the molecules HO−OH and H_2N-NH_2. The calculations show that free rotation cannot occur in either of these molecules at ordinary temperatures and that the only stable forms are those in which the azimuth of one-half of the molecule with respect to the other is approximately 90°. The essential feature of the argument is that the electrons of the two central atoms arrange themselves to form the strongest possible bonds and in so doing render the charge density on these atoms unsymmetrical about the axis of the molecule. The interaction of the two electronic clouds is the dominant factor in determining the azimuth of one group relative to the other; all other types of interaction have been estimated to shift the equilibrium position only slightly, i.e., probably from 90° to 100°.

Introduction

In a contribution[1] to the recent Faraday Society discussion on dipole moments we proposed, for the hydrogen peroxide molecule HOOH and the hydrazine molecule H_2NNH_2, forms which are highly unsymmetrical. We were led to our conclusions from a theoretical investigation of the electronic structures of these molecules, whence it appeared that the most important factor determining the azimuth of one-half of the molecule with respect to the other was the interaction of the two electronic clouds on the central atoms. It is the purpose of the present paper to describe the method of calculation rather than to discuss experimental facts which can be understood in the light of the final conclusions. The latter has been done already[1] and it was shown, for example, that the unsymmetrical forms of these molecules give a simple explanation of their large dipole moments and weak Raman spectra.

Two distinct methods have been developed for predicting the nuclear configuration of simple polyatomic molecules from a knowledge of the electronic configurations of the constituent atoms. These are known respectively as the method of electron pairs and the method of molecular orbitals and each has acheived a considerable measure of success. The strength of the former method lies in the fact that the energy of the polyatomic molecule is obtained directly as a sum of exchange integrals, the coefficients of a few of which depend on the angle parameters determining the configuration of the molecule. Although the magnitudes of the exchange integrals are not known accurately, yet from the way in which the various angle parameters appear in the energy expression, it is often possible to decide which is the most stable configuration for the nuclei. On the other hand, the orbital method involves the solution of a secular determinant of very high order, in which the magnitudes of the resonance integrals are uncertain and the angle parameters appear on and off the diagonal. Unless this secular equation can actually be solved, either exactly or by some approximate method, to give the energy of the molecule as a linear combination of resonance integrals with coefficients depending on the angle parameters, one cannot in general determine the most stable configuration. The orbital method is best applied to the calculation of energy states when the arrangement of the atoms in the molecule is already known, because then symmetry properties usually ensure sufficient factorization of the secular equation to render it soluble. In what follows, we are interested only in the relative energies of various configurations, rather than in the exact evaluation of the energy states of one particular configuration, and shall therefore employ the method of electron pairs.

[1] W. G. Penney and G. B. B. M. Sutherland, Faraday Society Discussion on Dipole Moments, Oxford, 1934.

Hydrogen Peroxide

The normal state of the oxygen atom is $(1s)^2(2s)^2(2p)^4\ ^3P$ but when the atom is in chemical combination with other atoms the L–S structure is partially destroyed. For accurate calculations on divalent oxygen one must therefore adopt wave functions which are linear combinations of those of ^3P, ^1D and ^1S. It is a very good approximation with oxygen, but not with carbon or nitrogen, to neglect the presence in the wave function of states obtained from the ground configuration by promoting, for example, an electron from the $2s$ to the $2p$ shell. This is because the greater stability which the molecular bonds would thus acquire is not capable of supplying sufficient energy for the promotion.

The four $2p$ electrons of an oxygen atom in the divalent state can have only one reasonable disposition. Two are taken with the same orbital wave function but with opposite spins; the other two are taken with their axes of quantization perpendicular to each other and to that of the first pair. The latter two can then be considered as having their spins free and ready to form bonds with electrons on other atoms. Hence the L–S structure of the oxygen atom affects the energy of the H_2O_2 molecule in a way which depends very little on the angle parameters. Since we are interested solely in determining the best values of these parameters, we shall neglect the L–S forces altogether and base our calculations simply on $(2p)^4$.

For convenience we shall append a suffix a to any quantity relating to one of the OH groups and a suffix b to those of the other (Fig. 1).

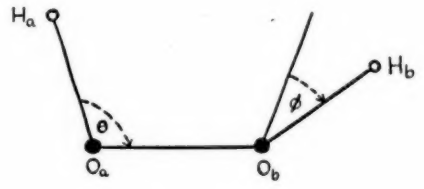

Fig. 1. The HOOH molecule.

Next, we take right-handed and left-handed sets of orthogonal axes (x, y, z) and (x', y', z') on O_a and O_b, respectively, with z and z' collinear but of opposite sense and with the xz plane containing H_a and the $x'z'$ plane containing H_b. Let ϕ denote the angle between the x and x' axes and θ stand for either of the equal angles $H_aO_aO_b$ or $H_bO_bO_a$.

The choice of paired wave functions[2] is then as follows:

$$\left.\begin{array}{ll} \psi_a(2p\sigma_z), & \psi_b(2p\sigma_{z'}); \\ \psi_a(2p\sigma_x), & \psi_{H_a}(1s); \\ \psi_b(2p\sigma_{x'}), & \psi_{H_b}(1s); \\ \psi_a(2p\sigma_y), & \psi_a(2p\sigma_y); \\ \psi_b(2p\sigma_{y'}), & \psi_b(2p\sigma_{y'}). \end{array}\right\} \quad (1)$$

Here, for example, $\psi_a(2p\sigma_z)$ means a $2p$ wave function located on the O_a nucleus, with $m_l=0$ referred to the z axis of quantization, and has the form $zf(r)$.

For the evaluation of the energy we have the well-known expression

$$W=\sum_{i,\,k} Q_{ik}+\sum_{i} J_{ii}-\tfrac{1}{2}\sum_{\substack{i,\,k \\ i\neq k}} J_{ik} \quad (2)$$

in which the J_{ii} terms arise from the exchange energy between two electrons forming a bond, while those denoted by $-\frac{1}{2}J_{ik}$ come from the exchange energy between two electrons in different bonds. The terms Q_{ik} are the ordinary Coulomb forces between electron i on one atom and electron j on another. It is necessary to introduce two types of diatomic integral, those in which one electron is on an oxygen atom and the other on a hydrogen atom, and those where both electrons are on oxygen atoms. These integrals have been defined and discussed elsewhere[3] but are repeated below for convenience.

$$\begin{aligned} Q_{\alpha\beta}&=\int\int \psi_H(s_1)\psi_a(\alpha_2)H'\psi_H(s_1)\psi_a(\beta_2)dv_1dv_2; \\ N_{\alpha\beta}&=-\int\int \psi_a(\alpha_1)\psi_H(s_2)H'\psi_b(\beta_2)\psi_H(s_1)dv_1dv_2 \\ Q_{\alpha\beta\gamma\delta}&=\int\int \psi_a(\alpha_1)\psi_b(\beta_2)H'\psi_a(\gamma_1)\psi_b(\delta_2)dv_1dv_2; \\ C_{\alpha\beta\gamma\delta}&=-\int\int \psi_a(\alpha_1)\psi_b(\beta_2)H'\psi_b(\gamma_1)\psi_a(\delta_2)dv_1dv_2. \end{aligned} \quad (3)$$

[2] We shall show later, when we come to consider the best value for θ, that some of the wave functions (1) have to be slightly modified in their directional properties. This correction may be disregarded for the present.

[3] W. G. Penney, Proc. Roy. Soc. **A144**, 166 (1934).

Here H' is the usual diatomic perturbative potential for the two nuclei appearing in the integral.

Although it is not a difficult matter to write down the energy W given by (2) in terms of the integrals (3), we shall confine our attention for the moment to that part of W which depends on ϕ. Thus we neglect interaction between atoms not coupled by bonds and disregard the terms due to van der Waals and ionic forces. Then θ is clearly $\pi/2$ and W can be written

$$W = \text{Const.} + \tfrac{1}{2}(C_{\pi\pi\pi\pi} - C_{\pi\pi'\pi'\pi}) \cos^2\phi + (D_{\pi\pi\pi\pi} - D_{\pi\pi'\pi'\pi}) \cos^2\phi.$$

The value of $(C_{\pi\pi\pi\pi} - C_{\pi\pi'\pi'\pi})$ has been given as 1.5 e.v. by Pauling and Wheland[4] and as 0.72 e.v. by one of the authors.[5] The sign of $(D_{\pi\pi\pi\pi} - D_{\pi\pi'\pi'\pi})$ is certainly positive, and according to Bartlett and Furry[6] is about equal in magnitude to $(C_{\pi\pi\pi\pi} - C_{\pi\pi'\pi'\pi})$. It is unfortunate that there is this uncertainty in the value of the coefficient of $\cos^2\phi$ but it is surely safe to assume that the change in W as ϕ varies from $\pi/2$ to 0 or π is not less than half a volt and is most probably around one volt. It only remains to be shown that the above is the dominant factor in determining the shape of the molecule, and that the contributions from steric repulsions, ionic interactions and van der Waals forces in favor of more symmetrical dispositions of the atoms are not sufficient to alter appreciably the value $\phi = \pi/2$ or to permit of free rotation about the O—O axis.

The expression for the energy of H_2O_2 is a function of the angles θ and ϕ and if a value of θ is postulated then the value of ϕ which makes W a minimum clearly depends on the value of θ chosen. However, the energy is not equally sensitive to changes in these angles, being much more affected by changes in θ than by changes in ϕ. This follows since the energy of the OH bond depends strongly on θ, having its minimum at $\theta = \pi/2$. To determine the values of θ and ϕ governing the most stable configuration we adopt a process of iteration, i.e., we choose a likely value of θ and, keeping it fixed, we determine the best value of ϕ. Then using this value for ϕ we try to verify whether our original assumption for θ is a good one.

Accordingly, let us for the moment make the rather naïve assumption that for all values of ϕ the net influence of H_b and O_b on H_a is the same as would be the steric repulsion on H_a of the other hydrogen atom in a water molecule containing H_a and O_a. The angle θ is then the angle of the water molecule, which evidence from several quarters[7] has shown to be between 100° and 110°. We shall use for the present the value employed by Theilacker[8] in his calculations on the electric moment of H_2O_2, *viz.* $\theta = 110°$. From the Morse function of Eyring and Polanyi[9] we can now estimate the steric repulsion between H_a and H_b as a function of ϕ, provided we neglect the partial migration of the hydrogen electrons to the oxygen nuclei. Assuming that the O—O and O—H distances are 1.4A and 1.0A, respectively, we arrive at the following values for the variation of the H_a—H_b steric repulsion with ϕ (Table I). By taking a value of

TABLE I.

$\phi°$	0	30	90	180
W e.v.	0.212	0.192	0.107	0.057

θ less than 110° it is found that these interactions become considerably larger, particularly near $\phi = 0$.

It might appear at first sight as though the interactions of H_a on O_b and of H_b on O_a would depend only on θ, but when one takes account of the fact that the density of electric charge around the oxygen atoms does not possess axial symmetry, it becomes evident that this interaction will also have a dependence on ϕ. The

[4] L. Pauling and G. Wheland, J. Chem. Phys. **1**, 362 (1933).

[5] W. G. Penney, Proc. Phys. Soc. London (1934).

[6] J. H. Bartlett, Phys. Rev. **37**, 507 (1931); W. Furry and J. H. Bartlett, Phys. Rev. **38**, 1615 (1931). Actually $D_{\pi\pi\pi\pi}$ is about twice as large as $C_{\pi\pi\pi\pi}$ with $\alpha = \kappa R = 5$, and about equal at $\alpha = 6$. The equilibrium value α of the O—O distance in H_2O_2 is probably about 6.

[7] R. Mecke *et al.*, Zeits. f. Physik **81**, 313, 445, 465 (1933); J. H. Van Vleck and P. C. Cross, J. Chem. Phys. **1**, 357 (1933).

[8] W. Theilacker, Zeits. f. physik. Chemie **B20**, 142 (1933).

[9] H. Eyring and M. Polanyi, Zeits. f. physik. Chemie **B12**, 279 (1933). We use, however, only 30 percent instead of 35 percent Morse function.

variation in W caused by this effect as ϕ changes from $\pi/2$ to 0 or π can readily be estimated from a table of integrals given by Ireland.[10] By denoting the angle $H_aO_bO_a$ by α, the required variation in energy may be written in Ireland's notation as

$$\delta W = \sin^2\alpha[2J_\Sigma(p^*p, bb) - 2J_\Pi(p^*p, bb) - K_\Sigma(pb, p^*b) + K_\Pi(pb, p^*b)],$$

where these integrals are to be evaluated at the H_aO_b distance. As shown later, the value of the effective internuclear distance R corresponding to this is very close to 5. At this value of R, the positions $\phi=0$ or π are only 0.04 e.v. more stable than the position $\phi=\pi/2$. This effect is therefore of minor importance.

Another type of interaction which contributes terms to the energy depending on ϕ is that arising from the mutual potential energy of the two OH dipoles. The evaluation of this effect by quantum mechanics is too difficult to be carried out here but it is easy to make a classical calculation which will give its approximate magnitude.[11] The dipole moment of the OH groups arises chiefly because some electronic charge migrates from its symmetrical position around the protons towards the oxygen nuclei. As an approximation we shall assume that the electric moment due to such a distortion of the electronic cloud may be represented by a point dipole situated two-thirds of the way along the OH line from the O atom and having its axis in the direction OH. Then applying the well-known formula for the mutual potential energy of two dipoles, we find that the variation of W with ϕ due to this effect is given by Table II. It is seen that the variation is not very large.

Summing up, we find that if θ is maintained at 110°, the variation of the energy with ϕ is represented by a curve similar to that shown in Fig. 2. The potential energy is greatest at $\phi=0$ (or $\phi=2\pi$ of course) because here the $2p\pi-2p\pi$ interactions between the electrons of the oxygen atoms, the interaction between dipoles and between H atoms, are all large. Only the lack of axial symmetry of oxygen charge density favors this position, and this effect is small. The secondary maximum at $\phi=\pi$ arises because the $2p\pi-2p\pi$ interaction is partially compensated by the low values of the other types of interaction. The heights of the maxima are perhaps one volt and half a volt, respectively. The best value of ϕ would appear to be somewhere between 90° and 100°; in our calculation[1] of the dipole moment of H_2O_2 we assumed the value 100°.

TABLE II.

ϕ°	0	90	180
W e.v.	0.280	0.180	0.139

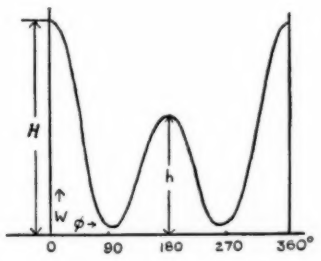

FIG. 2. The curve shows the variation in the energy of the HOOH molecule as the azimuth ϕ of one OH group to the other sweeps out the range $0\leq\phi\leq2\pi$. An exactly similar curve applies to the energy of the H_2N-NH_2 molecule. For HOOH the rough values of the maxima are $H=1.0$ e.v. and $h=0.5$ e.v., and for H_2N-NH_2, $H=0.33$ e.v. and $h=0.2$ e.v. The latter must be considered as more likely to be under- rather than overestimates.

The variation with θ

It is necessary now to investigate in greater detail the assumption that the best value of θ is 110° when ϕ is maintained at 90°, approximately its best value. To do this we consider separately the various terms in the energy depending on θ and find where their sum has its minimum. Before performing the calculations, however, we shall endeavor to explain the ideas underlying them. In the first place, if the

[10] C. Ireland, Phys. Rev. **43**, 329 (1933).

[11] A molecule where the dipole interaction may be important is $(CH_2OH)-(CH_2Cl)$. The dipole moment of this molecule has been found to be independent of temperature over a wide range. Zahn (Faraday Society Discussion on Dipole Moments, Oxford, 1934) accounts for this by assuming that the H atom of the OH group resonates between being attached to O and to Cl, thus holding the O and the Cl together. It seems more natural to suppose that it is the interaction of the two ionic groups which prevents free rotation in this molecule.

assumption of perfect pairing is made and all other interactions are neglected, θ has the value 90°. The repulsive interactions of O_b and H_b on H_a force H_a off the x-axis and thus increase θ. If the $\sigma-\sigma$ bond between the oxygen atoms were infinitely strong, the disposition of the bonding electrons on the oxygen atoms would remain unaltered, one having its axis of quantization along z and the other along x. Actually, however, the axis of symmetry of the electron which is bonded to that of H_a will tilt a little from the x-axis, say through an angle ψ_2, in order to preserve the O—H bonding energy as much as possible. Orthogonality conditions then require that the axis of symmetry of the other bonding electron of O_a also tilt through an angle ψ_2, this time from the z-axis. If we denote by ψ_1 the angle between the line H_aO_a and the axis of quantization of the electron of O_a which is coupled to that of H_a, we have (Fig. 3)

$$\theta=\pi/2+\psi_1+\psi_2.$$

The relation between ψ_1 and ψ_2 is determined by the relative strengths of the O—H and O—O bonds.

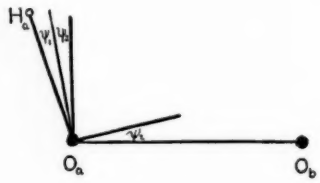

FIG. 3.

The dependence of W on ψ_1 and ψ_2 is given in the equation[12]

$$W=\text{Const.}+3(N_{\pi\pi}-N_{\sigma\sigma})\cos^2\psi_1 -3\cos^4\psi_2 C_{\sigma\sigma\sigma\sigma}/2+M(H_a, H_b) +2M(H_a, O_b)+I(a, b). \quad (4)$$

In this expression the second and third terms correspond respectively to the energies of the O—H and O—O bonds, while $M(H_a, H_b)$ represents the steric repulsion of the two H atoms and $2M(H_a, O_b)$ the steric repulsion of H_a on O_b and H_b on O_a. Finally $I(a, b)$ gives the interaction between the two OH dipoles.

[12] We have neglected certain C integrals, the values of which are very small.

Next we investigate the relation between ψ_1 and ψ_2. Since $C_{\sigma\sigma\sigma\sigma}$ is approximately equal to $(N_{\sigma\sigma}-N_{\pi\pi})$ and ψ_1 and ψ_2 are both small, (4) may be rewritten

$$W=\text{Const.}-3A(1-\psi_1^2)-3A(1-2\psi_2^2)/2+\cdots,$$

and as $(\psi_1+\psi_2)$ is fixed, this expression for W is clearly a minimum when $\psi_1=\psi_2$. Hence

$$W=\text{Const.}+6(N_{\sigma\sigma}-N_{\pi\pi})\psi^2+M(H_a, H_b) +2M(H_a, O_b)+I(a, b), \quad (5)$$

where $2\psi=\theta-\pi/2$. It now remains to evaluate the various terms in (5) and so find the value of θ for which W is a minimum.

The only term which offers any difficulty is $M(H_a, O_b)$ and the exact method by which it was obtained is described in the next paragraph. The function $M(H_a, H_b)$ was obtained simply from the Morse function of Eyring and Polanyi; the function $I(a, b)$ was obtained from the classical interaction of two dipoles; the value taken for $(N_{\sigma\sigma}-N_{\pi\pi})$ was 2.9 e.v.[13] Fig. 4 shows

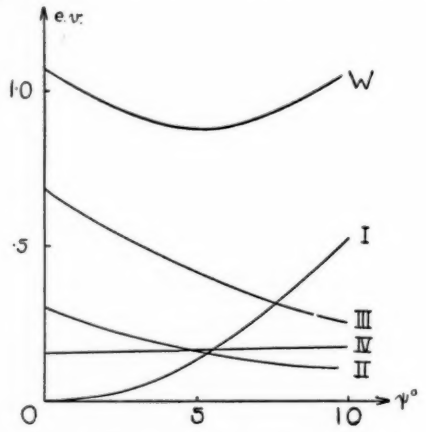

FIG. 4. The figure shows the variation in the energy W of the HOOH molecule with $\psi=(\theta-90)/2$. The best value of θ is seen to be 100°. The constituent parts of W as given in Eq. (5) are shown as I, II, III and IV, respectively.

the variation of the separate terms with θ, and the upper curve shows W. It is seen that the best value of ψ is about 5°, corresponding to $\theta=100°$.

The function $M(H_a, O_b)$

The energy of an OH molecule in terms of Ireland's integrals, to the approximation of (2) is

[13] J. H. Van Vleck, J. Chem. Phys. **2**, 20 (1934).

$$W(\mathrm{OH}) = 2J(ss, bb) + 3J_{\Pi}(p^*p, bb) + J_{\Sigma}(p^*p, bb) - K(sb, sb) - 3K_{\Pi}(pb, p^*b)/2 + K_{\Sigma}(pb, p^*b).$$

Using the table of integrals given by Ireland, we find that this has its minimum at $R = 2.63$. Now the O—H internuclear distance in the equilibrium position is known to be very nearly 1.0A and this gives us immediately the scale for R. Once again in terms of Ireland's integrals, the mutual energy of O_b and H_a in the position $\phi = \pi/2$ is

$$\delta W = [2J(ss, bb) + 3J_{\Pi}(p^*p, bb) + J_{\Sigma}(p^*p, bb) - K(sb, sb) - 3K_{\Pi}(pb, p^*b)/2 - K_{\Sigma}(pb, p^*b)/2] - \sin^2\alpha[J_{\Pi}(p^*p, bb) - J_{\Sigma}(p^*p, bb)] + \sin^2\alpha[K_{\Pi}(pb, p^*b) - K_{\Sigma}(pb, p^*b)]/2,$$

where α is the $H_aO_bO_a$ angle. The O_aH_b distance in Angstroms is readily determined for various values of θ from the known O—O and O—H distances and the corresponding values of R are obtained from the scale factor already discussed. The variation of δW with θ is then found by using the table of integrals given by Ireland. As one would expect, the expression of δW is very sensitive to changes in the O—O distance. Fortunately, however, θ is rather insensitive to such a variation in δW so that on the whole our estimate of θ has a range of uncertainty of only a few degrees.

As a criticism of the above calculations, it might be urged that the numerical values employed for the integrals give far too low an energy of dissociation for the water molecule. Thus Coolidge[14] finds from calculations similar in principle to those of Ireland, a theoretical value 3.5 e.v., assuming nonpolar wave functions, and 5.7 e.v. including polar terms, in contrast with the observed value 10 e.v. However, in our calculations on θ we are balancing various terms against each other and, as theoretical values are used throughout, it seems unlikely that our estimate $\theta = 100°$ is far out.

Hydrazine

Calculations can be made on hydrazine very similar to those already described for hydrogen peroxide. The two additional hydrogen atoms complicate matters to some extent but the chief difficulty arises from the fact that the $(2s)^2$ shell of the nitrogen atom shows a distinct tendency to break up under the influence of neighboring atoms. As a consequence, one has to deal not with a pure configuration $(2s)^2(2p)^3$ but with a mixture of $(2s)^2(2p)^3$ and $(2s)(2p)^4$. Although it is not possible to estimate the "coefficient of mixing" very accurately, yet its approximate value is readily perceived. As before, the L, S forces of the central atoms can be neglected since they have little to do with deciding the azimuth of one NH_2 group with respect to the other.

In a first attempt at constructing a model for the hydrazine molecule, one would naturally adopt for the three valencies of the nitrogen atom the three mutually orthogonal bonds of $(2p)^3$. Neglecting interactions between atoms not coupled by bonds, the molecule thus obtained would have the angles HNN, $H_1N_1H_2$, $H_3N_2H_4$, all 90°, and free rotation would occur about the N—N axis. However, when various types of steric repulsion are included, it is found that the interaction between the hydrogen atoms alone is sufficiently large to prevent free rotation at ordinary temperatures. In fact, the molecule is fixed quite firmly in the *trans* position, and in consequence this model has zero electric moment. The experimental observation[15] that the dipole moment is quite large (1.83×10^{-18}) can only mean that there exists a more stable configuration than the one described.

Consider one of the $2s$ electrons extracted from a nitrogen atom; there remains a configuration $(2s)(2p)^3$, identical with that of the tetravalent carbon atom. Now it is well known that the four valencies of the carbon atom are disposed tetrahedrally, and that their great bonding power arises from the hybridization of the $2s$ and the $2p$ wave functions.[16] If the $2s$ electron which was removed from the N atom is now restored, not into the $2s$ orbit but into one of the

[14] A. S. Coolidge, Phys. Rev. **42**, 189 (1932).

[15] L. F. Audrieth, W. Nespital and H. Ulich, J. Am. Chem. Soc. **55**, 673 (1933).

[16] The hybridization of the s and p wave functions in the N atom was first discussed (with reference to the NH_3 molecule) by J. H. Van Vleck, J. Chem. Phys. **1**, 219 (1933). The importance of the hybridization has been further emphasized by W. G. Penney, Proc. Roy. Soc. (1934).

already singly-occupied tetrahedral orbits, then an N atom is obtained with powerful valence bonds along three of the tetrahedral directions and with a pair of electrons of opposite spins occupying the fourth.[17] A hydrazine molecule constructed from such nitrogen atoms is the most stable one possible (Fig. 5). An alternative

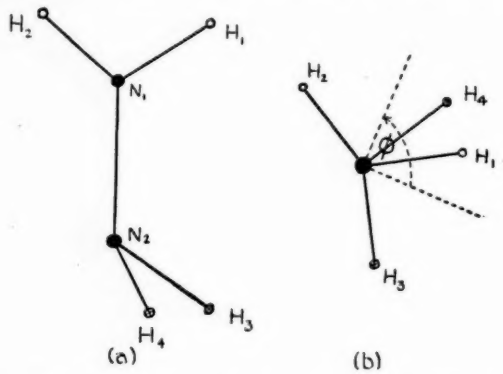

FIG. 5. Elevation (*a*) and plan (*b*) of the H_2N-NH_2 molecule.

way of picturing its formation is to imagine a hydrogen atom removed from each of two ammonia molecules and the two NH_2 residues coupled together along the line of their free valencies.

The tetrahedral wave functions can be written very simply as

$$\psi_t=\tfrac{1}{2}[\psi_N(2s)+(3)^{\frac{1}{2}}\psi_N(2p\sigma_t)],$$

where $\psi_N(2p\sigma_t)$ means a $2p$ wave function centered about the N atom with its axis of quantization along the tetrahedral direction t. Using such wave functions and adopting the pairing of spins in the way discussed above, we find that the dependence of the energy W on the azimuth ϕ is given by

$$W=K+4\cos^2\phi[(D_{\pi\pi\pi\pi}-D_{\pi\pi'\pi'\pi})+\tfrac{1}{2}(C_{\pi\pi\pi\pi}-C_{\pi\pi'\pi'\pi})]/9. \quad (6)$$

Here K represents the effect of steric repulsions, ionic interactions and van der Waals forces and includes as well terms of the C and D types with coefficients depending on ϕ, but whose magnitude compared with that of $C_{\pi\pi\pi\pi}$ or $D_{\pi\pi\pi\pi}$ is negligible. Just as with HOOH it can readily be shown that the second term in (6) is the dominant factor in determining the relative orientation of the two NH_2 groups. There is no essential difference in the method employed, i.e., the various interactions (steric, ionic, etc.) are estimated for different values of ϕ, assuming $\theta=110°$. In performing the calculations we employed for the N—N distance[18] the value 1.5A and for the N—H distance[19] the value 1.02A. The final result is that the equilibrium position $\phi=90°$ given by the second term of (6) alone is perhaps modified to $\phi=100°$. Thus the curve illustrating the dependence of W on ϕ is similar to that of Fig. 2 with $H=\frac{1}{3}$ volt and $h=\frac{1}{5}$ volt.

We wish to thank Professor T. M. Lowry for helpful discussion of the chemical aspects of the present paper.

[17] We do not wish to imply that the bonds are exactly at the (regular) tetrahedral angle 109.5°, nor that the disposition of the bonds and the angle parameters of the model are unmodified by the various steric repulsions, ionic interactions and van der Waals forces. However, for our purpose these are small corrections and can be ignored.

[18] This was estimated from Badger's formula (J. Chem. Phys. **2**, 218 (1934)), by using 900 cm^{-1} as an approximate value of the frequency corresponding to the symmetrical oscillation of the two halves of the NH_2-NH_2 molecule. Compare data on the Raman spectra of N_2H_4, Imanishi, Papers Inst. Tokyo **16**, 1 (1931); Sutherland, Nature **126**, 916 (1930).

[19] This is taken from Dennison and Uhlenbeck's determination of the dimensions of the NH_3 molecule from infrared data, Phys. Rev. **41**, 313 (1932).

The Dipole Moments of the Methyl and Ethyl Halides

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(Received May 21, 1934)

The dielectric constants of the vapors of the methyl and ethyl halides have been measured in order to obtain accurate values for their dipole moments. The increase in moment from the methyl to the ethyl halide accords with the previously advanced hypothesis of an inductive effect, but the change in the increase with change in the halogen involved points to the influence of an additional factor. The change in moment from compound to compound is compared with the change in the Raman frequency associated with the carbon-halogen bond.

BECAUSE of the importance of the dipole moments associated with the carbon-halogen bonds and because of interest in the effect of the carbon chain upon the moment of the molecule, it has seemed desirable to make accurate determinations of the moments of the methyl and ethyl fluorides, bromides and iodides in the vapor state, the chlorides having been previously so determined.[1] Moreover, results on the alkyl halides in solution gave abnormally high values for the atomic polarization, which suggested the possibility of a gradual increase in moment with rising temperature, a possibility requiring thorough investigation. Although the values reported by Mahanti[2] 2.00×10^{-18} for ethyl chloride and 2.03×10^{-18} for propyl chloride are in excellent agreement with the accurately determined values of Sänger and Fuchs, his value 2.00×10^{-18} for methyl chloride is considerably higher than the 1.86×10^{-18} found by both of these investigators. The similar identity which Mahanti reports in the cases of the methyl, ethyl and propyl bromides and the iodides is so different from the behavior found in solution[3] that his moment values could not be regarded as a basis for discussion.

The dielectric constants were measured with the apparatus previously described,[4] except that the gold-palladium cell used by Zahn[5] was employed in the measurements on ethyl fluoride and the iodides. As in earlier work,[6] the polarization P was calculated from the dielectric constant ϵ and the molar volume V as $P=[(\epsilon-1)/(\epsilon+2)]V$, the polarization-pressure curve at each absolute temperature T being extrapolated to zero pressure to obtain a value for use in the Debye equation, $P=a+b/T$. The value of the atomic polarization was calculated as $P_A=a-P_E$, the difference between a, the total induced polarization, and P_E, the molar refraction extrapolated to infinite wave-length. The dipole moments were calculated from the values of b as $\mu=0.01273\times10^{-18}(b^{\frac{1}{2}})$ and should be in error by no more than 0.01×10^{-18}.

PREPARATION AND PURIFICATION OF MATERIALS

Methyl fluoride

Methyl fluoride was prepared from potassium fluoride and potassium methyl sulfate by the method described by Bennett.[7] Different fractions of the material, even the first and last, gave polarization values differing by less than the error of measurement.

Ethyl fluoride

261 grams of mercurous fluoride prepared according to Ruff[8] and 207 grams of ethyl iodide, purified as described below, were allowed to react

[1] R. Sänger, Helv. Phys. Acta **3**, 161 (1930); Phys. Zeits. **32**, 20 (1931); O. Fuchs, Zeits. f. Physik **63**, 824 (1930).

[2] P. C. Mahanti, Phys. Zeits. **31**, 546 (1930).

[3] C. P. Smyth, *Dielectric Constant and Molecular Structure*, p. 102, New York, The Chemical Catalog Co., Inc., 1931.

[4] McAlpine and Smyth, J. Am. Chem. Soc. **55**, 453 (1933).

[5] C. T. Zahn, Phys. Rev. **24**, 400 (1924).

[6] Smyth and McAlpine, J. Chem. Phys. **1**, 190 (1933).

[7] W. H. Bennett, J. Am. Chem. Soc. **51**, 377 (1929).

[8] O. Ruff, *Die Chemie des Fluors*, p. 34, Berlin, Springer (1920).

under ordinary pressure in a vessel made of black iron pipe provided with suitable caps for the ends. The reaction vessel was maintained at about 70°, and the effluent gases were passed upward through a glass spiral surrounded by a toluene bath maintained at −35 to −30° in order to remove most of the ethyl iodide vapor carried along and then into a trap maintained at −78°, where the reaction product condensed. The 40 cc of liquid thus obtained was evaporated through long drying tubes of calcium chloride and phosphorus pentoxide and again condensed. This material was then given a series of fractionations between large traps, and the various fractions were tested for vapor pressure and polarization. The first fractions showed high vapor pressures because, apparently, of the presence of ethylene, but the later fractions, the last 5 cc having been discarded, had vapor pressures between 401.9 mm and 410.6 mm, corresponding to a boiling point range of less than 0.5°. The polarization values determined for three fractions within these limits showed no detectable differences. Two 5 cc fractions differing by 2.1 mm in vapor pressure were combined and measured to obtain the following vapor pressure values: −50.0°, 406.1 mm; −40.0°, 687.9 mm; −37.8°, 760 mm. The boiling point −37.8° thus obtained is considerably lower than the value −32° given by *International Critical Tables*, but it is believed that so large a discrepancy cannot arise from the small quantities of impurities presumably remaining in the material here measured, which is judged to be of satisfactory purity. Small quantities of the material obtained in previous preparations of inadequate yield had vapor pressures approximately equal to the values found for this large preparation.

Methyl bromide

Kahlbaum's material was passed through spiral wash bottles containing water and concentrated sulfuric acid, then through drying tubes filled with calcium chloride and phosphorus pentoxide, and finally was condensed in a trap. The polarizations of the first and last fractions of the material were identical within the limits of experimental error.

Ethyl bromide

Merck's C.P. material was shaken three times with concentrated sulfuric acid, once with water, once with 10 percent sodium carbonate solution, then three times with water. It was dried over two separate portions of calcium chloride, then over phosphorus pentoxide, and was finally fractionally distilled; b.p., 37.9–38.1°; n_D^{20}, 1.42443.

Methyl iodide

Merck's methyl iodide was shaken several times with portions of water, dried, first over calcium chloride, then over phosphorus pentoxide, and finally fractionally distilled; b.p., 42.6°; n_D^{20}, 1.53067.

Ethyl iodide

Ethyl iodide from the Sterling Products Company was shaken with mercury until the yellow color was gone, filtered, shaken repeatedly with fresh portions of water, dried, first over calcium chloride then over phosphorus pentoxide, and fractionally distilled; b.p., 72.4–72.6°; n_D^{20}, 1.51336.

Experimental Results

As a check upon the accuracy of the apparatus seven runs were made with air at 28.1°C and at pressures between 925 and 1122 mm. When reduced to 0° and 760 mm, they gave a mean value 581 for $(\epsilon-1)\times10^6$, identical with that found in the earlier measurements.[4] After the gold-palladium cell had been substituted for the copper cell and a larger fixed condenser introduced into the apparatus, ethyl bromide vapor was run at 412.2°K for comparison with the value obtained with the copper cell. The mean of seven determinations of the polarization, 81.96, was half a percent lower than the value 82.38 previously obtained with the copper cell, a difference so small as to affect the moment value by no more than 0.005×10^{-18}.

The error in the polarization values caused by the use of the ideal gas law in their calculation is eliminated by the extrapolation to zero pressure to obtain the values of P_0 given in Table I. The polarization-pressure curve at these pressures is a straight line, usually obtained by plotting six or eight polarization values at each temperature

TABLE I. *Polarization values.*

T, °K	P_{500}	P_0	T, °K	P_{500}	P_0
Methyl fluoride			Ethyl bromide		
224.0	99.84	98.20	303.4	106.0	104.2
237.4	95.14	93.90	306.6	105.2	103.5
252.4	89.04	87.94	352.3	93.64	92.70
272.7	83.66	83.12	394.7	86.04	84.90
301.2	76.74	76.40	441.4	78.4	78.4
334.1	69.86	69.68			
380.3	62.38	62.26	Methyl iodide		
414.3	57.70	57.60	304.7	73.80	71.82
451.0	53.66	53.60	313.4	71.95	70.15
498.1	49.40	49.37	345.9		65.3
			398.6		59.4
Ethyl fluoride			446.7		55.5
236.2	108.5	107.3	494.4		51.8
298.4	88.88	88.60			
328.8	81.62	81.34	Ethyl iodide		
372.5	73.37	73.26	348.3	92.05	89.95
422.0	65.90	65.90	411.4	81.00	79.40
480.8	59.26	59.26	434.3	78.44	77.15
534.6	54.14	54.14	463.2	74.60	74.00
Methyl bromide					
306.2	80.98	79.60			
309.1	80.18	78.85			
330.8	75.57	74.40			
368.0	69.16	68.40			
405.9	64.12	63.85			

against the pressures at which they are determined. The course of each curve is shown by giving as P_{500} the polarization value at 500 mm, sometimes obtained by extrapolation. In the case of methyl iodide, the values of P_{500} are omitted at the higher temperatures where the slopes of the curves are uncertain. As the temperature rises, the decreasing difference between P_{500} and P_0 shows the decreasing deviation of the vapor from ideal behavior, the difference often being undetectable at the highest temperatures measured. The P_0 values are used to calculate by the method of least squares the constants given in Table II. The values of a and μ for methyl and ethyl chloride are the means of those obtained by Sänger[1] and Fuchs.[1] The last column of Table II gives the increase in moment from the methyl to the corresponding ethyl halide.

DISCUSSION OF RESULTS

The atomic polarizations of these substances, with the exception of ethyl fluoride, have been included in the discussion of the problem of atomic polarization in an earlier paper,[9] where

TABLE II. *Constants of methyl and ethyl halides.*

	a	P_E	P_A	b	$\mu\times10^{18}$	$(C_2H_5-\!-CH_3-)\times10^{18}$
CH_3F	8.95	6.6	2.4	20170	1.808	
C_2H_5F	14.04	11.1	2.9	22760	1.92	0.11
CH_3Cl	13.6[1]	12.0	1.6		1.86[1]	
C_2H_5Cl	19.3[1]	16.6	2.7		2.03[1]	.17
CH_3Br	15.40	14.2	1.2	19580	1.78	
C_2H_5Br	21.49	18.6	2.9	25080	2.02	.24
CH_3I	20.22	18.5	1.7	15650	1.59	
C_2H_5I	25.71	23.3	2.4	22290	1.90	.31

[9] C. P. Smyth, J. Chem. Phys. **1**, 247 (1933).

they served to prove the incorrectness of some abnormally high values obtained from measurements on liquids. A revision of the data has altered a number of the values somewhat, increasing the accuracy sufficiently to make apparent an increase in P_A from the methyl to the ethyl compound in accordance with the general tendency previously observed[10] for an increase in P_A with increase in the number of atomic nuclei or groups in the molecule.

The decrease in moment from the chloride to the iodide is much less pronounced than in the case of the hydrogen halides, for which the values are 1.03, 0.78, and 0.38×10^{-18} for HCl, HBr and HI, respectively.[5] This rapid decrease in the hydrogen halides, in spite of the increased nuclear separation, is undoubtedly due to the increased shift of negative charge toward the positive because of the increasing polarizability of the halogen.[11] As the positive charges of the methyl group are not as near to the negative charges of the halogen as is the proton in the hydrogen halides, the displacement of the negative charges should be smaller in the methyl halides so that the moments should fall off less rapidly with increasing halogen polarizability. A rough value 0.8×10^{-18} may be calculated for HF by assuming the ratio of the HF moment to the observed HCl moment to be equal to the ratio of the moment values calculated by Kirkwood[12] for these two molecules. Although this value may be too approximate to be significant, it is interesting to note that it is lower than the HCl moment, while the values for methyl and ethyl fluoride are also slightly lower than those for the corresponding chlorides.

It is obvious that there are, at least, two opposing factors determining the moments. Increase in the carbon-halogen distance should tend to increase the moment, while increase in the halogen polarizability should decrease it. It appears that the 0.35A increase in the distance between the carbon and halogen nuclei from the fluoride to the chloride more than compensates for the increase in halogen polarizability, while the effects of the smaller increases in nuclear separation, 0.15A from the chloride to the

[10] C. P. Smyth, J. Am. Chem. Soc. **51**, 2051 (1929).

[11] C. P. Smyth, Phil. Mag. **47**, 530 (1924).

[12] J. G. Kirkwood, Phys. Zeits. **33**, 259 (1932).

bromide and 0.19A from the bromide to the iodide, are overbalanced by the greater electronic shifts permitted by greater polarizability. The decrease in moment produced by changing from one halogen to the next larger increases by $0.12 \pm 0.01 \times 10^{-18}$ for each change in going down the series from fluoride to iodide in both the methyl and the ethyl halides. Thus, the difference between $CH_3F - CH_3Cl = -0.05$ and $CH_3Cl - CH_3Br = 0.08$ is -0.13 and the difference between $CH_3Cl - CH_3Br = 0.08$ and $CH_3Br - CH_3I = 0.19$ is -0.11. The difference between the corresponding methyl and ethyl halides increases by 0.07×10^{-18} with each change from one halogen to the next larger.

It was shown years ago[3, 13] that the greater moment of an ethyl halide as compared to a methyl was presumably due to the moment induced in the second carbon by the principal dipole in the carbon-halogen bond. Beyond this second carbon the effect of induction is practically negligible as far as the moment is concerned since higher primary alkyl halides were found to be practically indistinguishable in moment from the ethyl compound, a result confirmed in the case of the chlorides by Sänger's[1] value 2.04×10^{-18} for propyl chloride vapor and a value 2.04×10^{-18} for butyl chloride vapor shortly to be published from this laboratory. However, a secondary alkyl halide has been found to have a larger moment than a primary, while a tertiary has one still larger, indicating that, when additional carbons are brought within the effective field of the principal carbon-halogen dipole, measurable moments are induced upon them. A branch farther along the chain, as in an isobutyl halide, does not increase the moment, the field due to the principal dipole being apparently insufficient to induce a detectable moment in these more remote carbons.

The precise location of the principal dipole in the carbon-halogen bond is not known, but it has seemed reasonable to locate it 7/8 of the distance from the carbon nucleus to the halogen nucleus[14] and calculations of induced moments based on this assumption have given good agreement with observed values.[6] The distance of the principal dipole from the second carbon of the ethyl halide should increase with increasing size of the halogen and its inductive effect upon the charges of this carbon should, therefore, decrease unless the principal dipole itself increases. Although a rough calculation of this principal dipole moment gave 0.91 and 1.15×10^{-18} for methyl fluoride and methyl chloride,[6] a similar calculation gives 1.18 for the bromide and 1.14×10^{-18} for the iodide. The increasing methyl-ethyl difference with increasing halogen size is, therefore, contrary to what would be predicted on the basis of inductive effect and indicates that some other factor must play a part.

It is interesting to note qualitative analogies and differences between the alkyl halide moments and the Raman frequencies associated with the carbon-halogen bonds.[15] The frequency which probably corresponds to a longitudinal vibration in the carbon-halogen line drops from the methyl to the ethyl and remains constant as the carbon chain is lengthened from two to five atoms just as the moment remains constant in the case of the chlorides after a rise from methyl to ethyl. A secondary chloride shows a further decrease in frequency and increase in moment and a tertiary chloride a still further decrease in frequency and increase in moment. Branching of the chain at the second carbon increases the Raman frequency, but, as far as can be judged from measurements on the liquid, leaves the dipole moment identical with that of the normal compound. Branching of the chain at the third carbon or beyond in the halides leaves both the Raman frequency and the moment unaffected. Generally, in these compounds, decrease in frequency appears to accompany increase in moment. However, the decrease in frequency from methyl to ethyl becomes smaller with increasing halogen size, in part, at least, a mere mass effect, while the increase in moment becomes greater.

The writers wish to thank Dr. Albert L. Henne of Ohio State University for advice on the preparation of ethyl fluoride and to express their indebtedness to the National Research Council for a grant-in-aid, which has made possible the completion of a portion of this investigation.

[13] C. P. Smyth and H. E. Rogers, J. Am. Chem. Soc. **52**, 2227 (1930); C. P. Smyth and R. W. Dornte, ibid. **53**, 545 (1931).

[14] L. Meyer, Zeits. f. physik. Chemie **B8**, 27 (1930).

[15] W. D. Harkins and H. F. Bowers, J. Am. Chem. Soc. **53**, 2425 (1931); W. D. Harkins and R. R. Hann, ibid. **54**, 3920 (1932).

The Kinetics of the Homogeneous Thermal Decomposition of Ethyl Ether at Pressures up to Two Hundred Atmospheres

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(Received May 28, 1934)

A new and simple apparatus is described by means of which it is possible to investigate the kinetics of homogeneous gas reactions up to pressures of several hundred atmospheres. With this apparatus the decomposition of gaseous ethyl ether has been investigated at 426°C over the pressure range 2000 to 14,500 cm. The rate of reaction increases rapidly with pressure up to 10,000 cm and then increases more slowly. The rate at 14,500 cm is approximately 50 times greater than the previously assumed value at infinite pressure. It is shown that by assuming that the number of degrees of freedom involved varies with the time between molecular collisions it is possible to explain these results. Further investigations are in progress.

Introduction

A REACTION may be quite definitely designated as unimolecular, the rate constants of which show a characteristic behavior in that they tend to a constant value as high pressures are approached, but fall in value as one goes to low pressures. "As a matter of fact," to quote O. K. Rice,[1] "in many cases . . . this is a statement of theoretical expectation rather than an experimental fact, since the limiting high pressure rate has not been reached experimentally." It was therefore considered to be of interest to extend the range of experimental investigation to as high a pressure as possible.

According to the Hinshelwood theory[2] (theory I)[3] of homogeneous unimolecular reactions, on plotting $1/k$ against $1/P$ a straight line with an intercept at $1/k_\infty$ should be obtained. The theories of Rice and Ramsperger[4] (theory II) and of Kassel[5] (theory III) demand a curved plot, the curvature being greatest when the number of squared terms involved is large. However, the latter two theories depend, for their complete verification, in by far the majority of cases, upon an extrapolation to the high pressure rate based upon theory I, i.e., a linear extrapolation of $1/k$ against $1/P$ is used although this is almost certainly incorrect. It is therefore very desirable to approximate experimentally as closely as possible to the high pressure rate.

The localized energy theories (II and III) also predict different Arrhenius heats of activation at low and high pressures. While the difference in energies of activation may be too small to be evaluated experimentally in most cases, the general result predicted is that the rate should fall off more rapidly at higher temperatures as the pressure is lowered; this effect should be most pronounced with large values of n.

A further possibility attendant upon increasing the experimental pressure range has been pointed out by O. K. Rice.[6] Over an extended pressure range it may be possible to have several transitions from unimolecular to bimolecular rates in the case of a complex molecule. Fletcher and Hinshelwood[7] also bring forward evidence indicating the possibility of several activated states for a given molecule, these different activated states having different transformation probabilities.

There are, then a large number of inducements for extending the pressure range of kinetic measurements. Experiments at low pressures have yielded results of great importance, and high pressure rate measurements may reveal further material of theoretical value.

[1] Rice, J. A. C. S. **54**, 4558 (1932).
[2] Hinshelwood, Proc. Roy. Soc. **A113**, 230 (1926).
[3] This method of identification of current theories follows the usage of Rice and Ramsperger.
[4] Rice and Ramsperger, J. A. C. S. **49**, 1617 (1927).
[5] Kassel, J. Phys. Chem. **32**, 225 (1928).
[6] Rice, Zeits. f. physik. Chemie **B7**, 226 (1930).
[7] Fletcher and Hinshelwood, Proc. Roy. Soc. **A141**, 41 (1933).

At the time this investigation was initiated some work had already been done in what may be termed the high pressure range. Kistiakowsky[8] investigated the hydrogen iodide decomposition at concentrations up to seven moles per liter. Nagasako and Volmer[9] followed the effect of pressure on the kinetics of the decomposition of nitrous oxide up to 800 cm, the reaction being found to remain unimolecular as the pressure was increased. Newitt and Vernon[10] reported an investigation of the decomposition of diethyl ether at pressures up to 17 atmospheres, but aside from suggesting a chemical mechanism drew no theoretical conclusions from their work. Coffin and Geddes[11] have recently reported a study of the transition from paraldehyde to acetaldehyde over a range extending from a few millimeters to eighteen atmospheres; they find a rather unexpected decrease in rate with increased pressure.

Apparatus

The apparatus finally devised is extremely simple in principle. A quantity of the reactant is introduced by distillation into a steel reaction vessel which is connected to a pressure measuring device by steel capillary tubing, the gas pressure being transmitted to the gauge through a liquid. The course of the reaction is then followed by observing the change of pressure with time.

The complete assembly is shown in Fig. 1, and the detailed construction of the reaction vessel in Fig. 2.

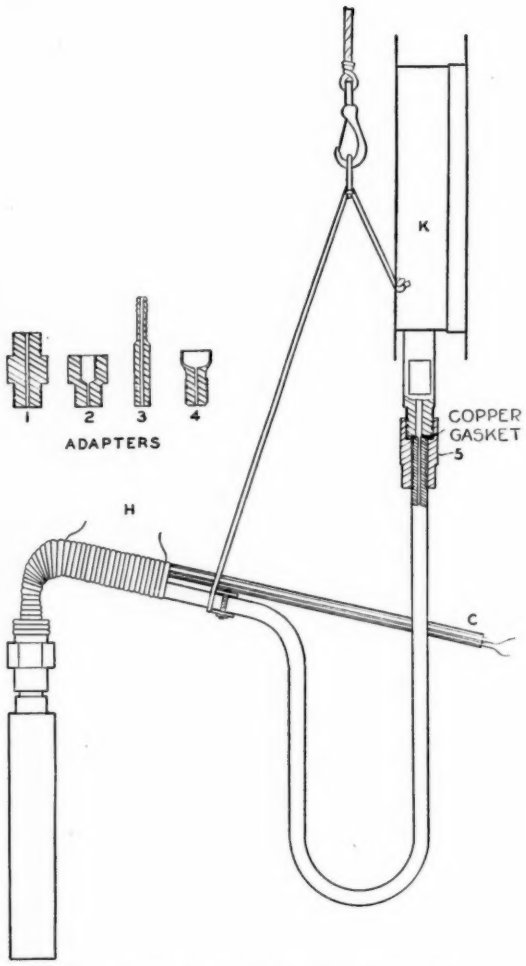


FIG. 1. Reaction vessel complete assembly.

Reaction vessel

A cylindrical bar of "Stabrite" stainless steel 8 inches long and 1.5 inch external diameter was drilled to a depth of 7.5 inch, the bore being 0.75 inch in diameter. The upper end of the hole was widened to 1 inch diameter and tapped to take a stainless steel adapter. This adapter (part 5, Fig. 2), after being seated firmly was welded into place, particular care being taken to ensure the absence of slag holes in the weld. The emergent end of the adapter had a 0.25 inch bore and was machined down to 0.5 inch diameter. The upper surface was scored with a circular 60° V-groove. The volume of the bomb was 47 cc.

The method of coupling the bomb to the tubing was a modified form of that employed by the Fixed Nitrogen Research Laboratory (U. S. Department of Agriculture).[12] A small collar of stainless steel was made to screw on the tubing end. A union nut of machine steel was then screwed down tightly on the adapter as indicated, drawing the tubing and adapter ends firmly together and thus compressing the inserted annealed copper gasket. The copper flowed into the V-groove on the adapter end, and into a

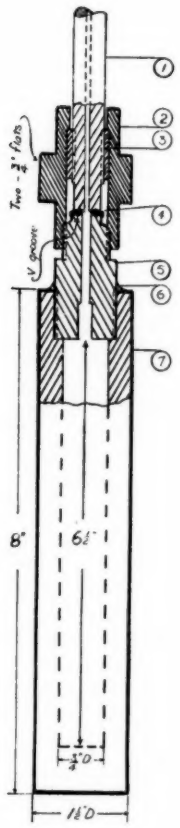
[8] Kistiakowsky, J. A. C. S. **50**, 2315 (1928).

[9] Nagasako and Volmer, Zeits. f. physik. Chemie **B10**, 414 (1930).

[10] Newitt and Vernon, Proc. Roy. Soc. **A135**, 307 (1932).

[11] Coffin and Geddes, J. Chem. Phys. **2**, 47 (1934).

[12] Curtis, *Fixed Nitrogen*, p. 267, New York, Chemical Catalog Co. (1932).



Item No.	Name of Part	Material
(1)	Tubing	Stainless Steel
(2)	Union Nut	Mach. Steel
(3)	Threaded Collar	Stainless Steel
(4)	Gasket	Annealed Copper
(5)	Adapter	Stainless Steel
(6)	Weld	Stainless Steel
(7)	Bomb	Stainless Steel

FIG. 2. Details of reaction vessel.

similar groove scored on the tubing end, and so formed a gas-tight joint. No part of the union was then exposed to the gas pressure. Difficulty was encountered, due to lack of suitable equipment, in scoring the tubing end uniformly, and also in providing perfectly plane surfaces on the two ends to be brought together. It was found necessary on this account to exert exceptional force on an 18 inch spanner in order to effect a gas-tight joint.

Tubing

The stainless steel tubing was made to specifications (by the Summerill Tubing Co.), 0.5 inch external diameter and a capillary bore of approximately 0.05 inch. The tubing was bent cold into the shape indicated in Fig. 1. The end of the tubing affixed to the bomb has been described; the other end which formed one arm of a U-bend was threaded to take an adapter, 5, made of machine steel with two 0.75 inch milled flats. This adapter was tapped so as to take any one of several adapting units or a Bourdon gauge.

At the end towards the bomb the tubing was wound with a small nichrome heating element. Insulated from this by a few turns of asbestos rope was placed a thermocouple junction enclosed in a Pyrex tube, *C*. The thermocouple and heating element were then tightly wrapped with several turns of asbestos rope as indicated at *H* in Fig. 1.

Gauges

Bourdon gauges were used to follow the change of pressure during the reaction. Two Crosby, 8.5 inch dial, AIH gauges were employed: One was graduated in 20 lb. units from 0 to 1500 lbs./sq. inch, the other was graduated in 100 lb. units from 0 to 5000 lbs./sq. inch. When in use their tubes, made of rust resistant steel, were filled with butyl phthalate.

The gauges were guaranteed by the manufacturers to be accurate to within 1 percent of the maximum graduation at any part above the first 5 percent of the scale. In practice the first 15 percent of the scale was seldom used. In order to calculate rate constants only a series of differences in pressure over a comparatively short range were required. It was therefore considered justifiable to assume that the true difference between any two readings in a single run was equal to the difference indicated by the gauge within the limits set by other sources of experimental error. Since rate measurements checked well within the possible experimental error, it was not deemed necessary to recalibrate the gauges. As a matter of interest, however, the low pressure gauge was checked against the vapor pressure of carbon dioxide at 0°C and 20°C; the pressures indicated were 515 and 835 lbs./sq. inch, respectively, checking well with the accepted values ((I.C.T.) of 506 and 831 lbs./sq. inch.

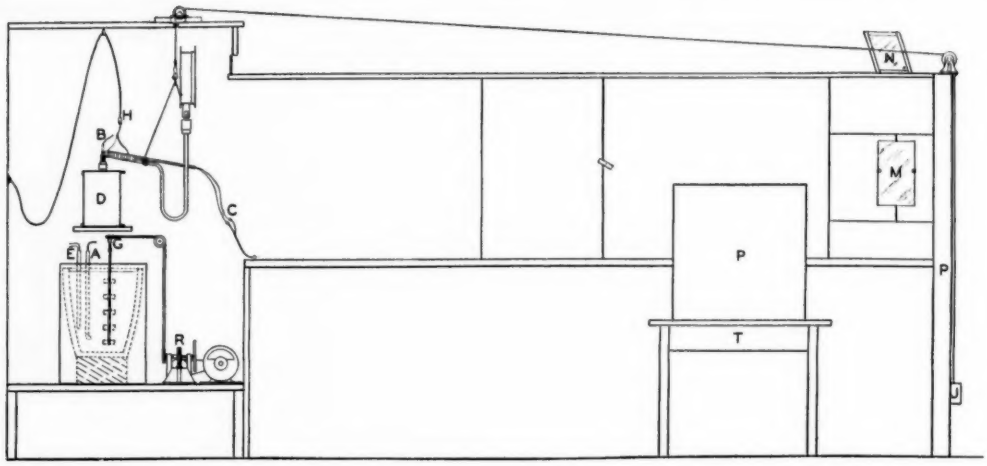


FIG. 3. Complete apparatus.

As has been frequently pointed out, Bourdon gauges tend to "creep" with long use, and periodic recalibration is necessary. During the period of this research, however, neither of the gauges was in operation for a total time exceeding 50 hours, and only seldom were they subjected to more than 75 percent of the maximum dial reading.

Experimental procedure

The bomb assembly was connected with a glass filling system through a rubber stopper and a cup shaped metal adapter. The reaction vessel was then cooled in an acetone-carbon dioxide mixture, and purified ethyl ether was introduced by distillation. This was followed by a thread of mercury which filled the steel capillary tubing to the bend next the bomb. The U-bend was then cooled, freezing the mercury, and butyl phthalate run in above the mercury.

The bomb assembly was then removed from the filling unit, the gauge was screwed tightly into place, and the entire unit suspended as indicated in Fig. 3. The bomb was placed in the pre-heating furnace *D*, which was constructed from a hinged organic combustion furnace and fitted around the bomb. The bomb was preheated to a temperature about 50° below that at which reaction takes place at an appreciable rate. The heating element *H* was kept about 50° above the critical temperature of the reactant in order to prevent the formation of a liquid phase during the reaction. The temperatures of the furnace *D* and the heater *H* were followed by a furnace pyrometer.

From this stage on all manipulations were made by the operator seated facing the plate glass mirror *M*, and protected by a stout housing of $\frac{3}{4}$ inch planks fitted with laminated safety glass windows. During the pre-heating period the acetone-carbon dioxide mixture surrounding the U-bend warms up until the mercury in the capillary melts, allowing the pressure being built up in the bomb to register on the gauge. When the pressure reading has reached its maximum constant value, the air furnace is swung open. Simultaneously the counterweight *J* is gently given an upward impetus and a portion of the weight removed. The bomb sinks rapidly into a six liter bath of molten lead until only the union nut appears above the surface. Pressure readings are then taken at frequent time intervals by means of a telescope directed at *M*.

When the bomb is first introduced the temperature of the lead bath drops several degrees, but within a minute the temperature may be brought to the desired equilibrium value. On account of the high heat capacity of the lead, fluctuations in temperature are reduced to a minimum, a constancy of ± 1°C being maintained by manual control throughout a run. The temperature of the bath was measured by means of a chromel-alumel thermocouple and could be read to about 0.2°C.

When a run had progressed sufficiently to give all the desired information, the bomb assembly was withdrawn from the lead bath and allowed to cool in the air. The bomb was then cooled in an acetone-carbon dioxide mixture, and when the pressure had dropped to 600 lbs. per sq. inch or less the mercury in the U-bend was frozen and the gauge removed. If the products of the reaction were to be discarded, the bomb was inverted and, when the mercury melted, the gas pressure forced out the mercury and butyl phthalate in the capillary. If it was desired to collect the products of reaction for analysis they were allowed to enter an evacuated two liter flask through a steel needle valve. The bomb and capillary were then rinsed out with ether prior to making another run.

Experimental Results

Pressure-time data for runs at various pressures are given in Table I and are plotted in Fig. 4.

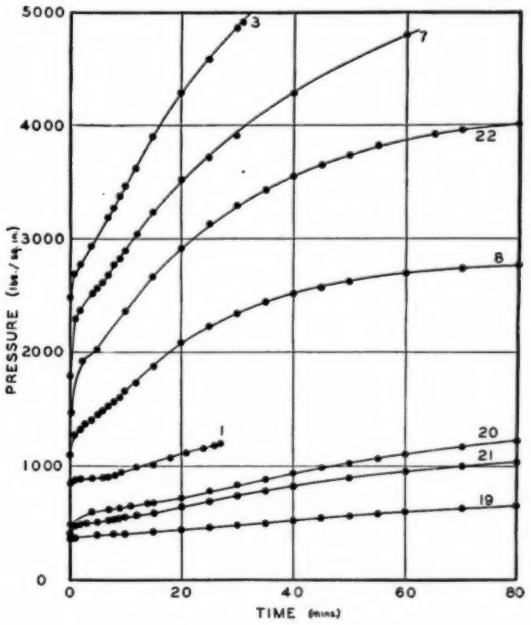


Fig. 4. Pressure-time curves.

Table I. *Pressure-time data for runs at various pressures.* I, time in minutes; II, pressure, lbs./sq. in.

A		B		C		D		E		F		G		H	
I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II
0	350	0	410	0	490	0	850	0	1100	0	1470	0	1800	0	2490
1	380	1	480	2.25	595	1	885	1	1280	2	1930	1	2300	1	2690
2	385	2	490	4	600	2	890	2	1325	3	1950	2	2390	1.5	2750
5	395	3	500	5.5	605	4	900	3	1370	5	2030	4	2520	2	2780
10	405	5	510	7	620	6	900	4	1405	10	2370	5	2570	2.75	2840
15	422	7	525	9	635	7	910	5	1455	15	2670	6	2620	4	2940
20	440	10	550	11	650	8	925	7	1530	20	2920	7	2680	5.75	3090
30	480	15	590	15	680	10	950	10	1660	25	3130	8	2780	7	3195
40	520	20	640	25	780	12	990	15	1890	30	3300	9	2830	8	3280
50	560	30	740	35	890	15	1000	20	2090	35	3440	10	2900	9	3380
60	595	40	822	50	1025	18	1075	30	2355	40	3560	12	3045	10	3470
80	660	70	998	70	1165	21	1100	40	2520	45	3660	15	3240	12	3630
100	715	100	1087	90	1265	24	1150	60	2690	50	3740	20	3535	15	3900
120	760	120	1130	110	1335	25	1175	80	2775	55	3830	25	3720	20	4290
180	845	∞	1320	130	1385	26	1200	100	2810	60	3865	30	3900	25	4590
∞	1020			150	1420			120	2865	65	3915	60	4795	30	4870
				170	1450			180	2920	70	3950			31	4910
				190	1470			225	2950	∞	4140				
				220	1500			∞	3140						

A. Initial pressure = 26.9 atm.; reaction vessel *C*; temperature 426°C; $k = 1.1 \times 10^{-4}$ sec.$^{-1}$. **B.** Initial pressure = 34.4 atm.; reaction vessel *C*; temperature 424.5°C; $k = 2.5 \times 10^{-4}$ sec.$^{-1}$; $k_{426} = 2.7 \times 10^{-4}$ sec.$^{-1}$ (calc.). **C.** Initial pressure = 40.8 atm.; reaction vessel *C*; temperature 424°C; $k = 2.7 \times 10^{-4}$ sec.$^{-1}$; $k_{426} = 3.0 \times 10^{-4}$ sec.$^{-1}$ (calc.). **D.** Initial pressure = 61 atm.; reaction vessel **A**; temperature 426.5°C; $k = 4.0 \times 10^{-4}$ sec.$^{-1}$; $k_{426} = 3.9 \times 10^{-4}$ sec.$^{-1}$ (calc.). **E.** Initial pressure = 92 atm.; reaction vessel *A*; temperature 428°C; $k = 7.1 \times 10^{-4}$ sec.$^{-1}$; $k_{426} = 6.4 \times 10^{-4}$ sec.$^{-1}$ (calc.). **F.** Initial pressure = 121 atm.; reaction vessel *C*; temperature 426°C; $k = 6.7 \times 10^{-4}$ sec.$^{-1}$. **G.** Initial pressure = 167 atm.; reaction vessel *A*; temperature 425°C; $k = 6.3 \times 10^{-4}$ sec.$^{-1}$; $k_{426} = 6.7 \times 10^{-4}$ sec.$^{-1}$ (calc.). **H.** Initial pressure = 190 atm.; reaction vessel *A*; temperature 424°C; $k = 6.3 \times 10^{-4}$ sec.$^{-1}$; $k_{426} = 6.9 \times 10^{-4}$ sec.$^{-1}$ (calc.).

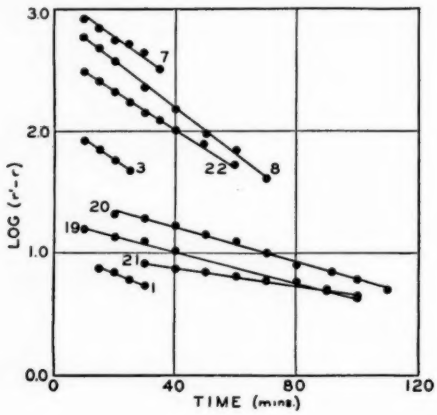


FIG. 5. Results plotted according to Guggenheim method.

The rate constants have been calculated directly from the pressure-time readings using the method of Guggenheim,[13] which is particularly suitable since it requires knowledge neither of the initial pressure nor of the initial time. The linearity of the curves in Fig. 5 shows the applicability of the method. The method has been applied to find the initial rate constant with reference to fractional pressure increase, rather than a rate constant which might be calculated therefrom by correcting for the number of moles of gas formed per mole of ether decomposed. The method by which the true rate constants are obtained from these values is described later. The experiments have varied slightly as to temperature, ranging from 424 to 428°C. In order to bring all to a common basis for comparison, the rate constants have been recalculated to 426°C by assuming an energy of activation of 53,000 calories per gram molecule. Since, at most, the correction is made for 2°C, the error that may be introduced is negligible even if the energy of activation assumed is erroneous in the region under investigation.

For the purpose of plotting rate against pressure an approximation to the initial pressure must be made. When the pressure readings of an individual run are plotted against time it is found that the curve (Fig. 6) obtained is divided into three more or less distinct portions. The first portion may be attributed to the thermal

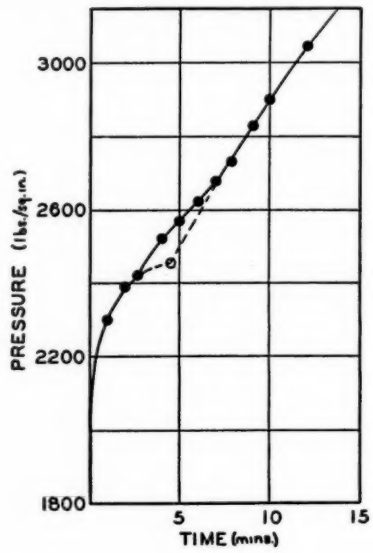


FIG. 6. Determination of initial pressure.

increase in pressure of the gas on passing from the pre-heating temperature to the temperature of the lead bath; this portion is characterized by a rapid increase of pressure which gradually decreases in rate. During the next few minutes the rate of increase of pressure picks up again, this being due to the reaction process starting while the superimposed thermal increase is drawing to a close. Finally the curve smooths out again and becomes a purely logarithmic rate curve. To determine the initial pressure a sufficiently accurate approximation may be made by extrapolating the pure reaction curve until it meets the extrapolated thermal expansion curve.

COMPARISON OF RESULTS AT HIGH AND LOW PRESSURES

The decomposition of diethyl ether was first studied by Hinshelwood.[14] His rate measurements have since been confirmed by Steacie[15] and by Kassel[16] within a range of one or two degrees in the absolute temperature scale. Hinshelwood represents the rate by the equation

[13] Guggenheim, Phil. Mag. **7**, 538 (1926).

[14] Hinshelwood, Proc. Roy. Soc. **A114**, 84 (1927).

[15] Steacie, J. Phys. Chem. **36**, 1562 (1932); J. Chem. Phys. **1**, 313 (1933).

[16] Kassel, J. A. C. S. **54**, 3641 (1932).

$$\ln k = 26.47 - 53{,}000/RT.$$

Kassel[17] finds, on recalculation of Hinshelwood's data, that the results may be more satisfactorily given by

$$\ln k = 26.35 - 53{,}000/RT.$$

O. K. Rice and Sickmann[18] have published a preliminary note on rate measurements at low pressures (0.15 to 490 mm), and find an activation energy of about 60,000 calories compared to Hinshelwood's 53,000. They also report tentatively the appearance of a second unimolecular reaction at these low pressures. Newitt and Vernon[19] have extended the measurements up to a pressure of about 17 atmospheres. Their results indicate an energy of activation approximately equal to that found by Hinshelwood.

Hinshelwood gives the following equation as representing the main reaction over the range 150 to 500 mm:

$$C_2H_5OC_2H_5 = 2CH_4 + 0.5C_2H_4 + CO.$$

This would indicate a pressure increase of 250 percent, but Hinshelwood found the pressure increase in general to be about 188 percent; at lower pressures the increase may have been somewhat larger, approaching 210 percent, although the experimental accuracy was insufficient to establish this definitely.

Newitt and Vernon in the pressure range from 3 to 14 atmospheres found the pressure increase to be 175 ± 2 percent. They interpret their results, in the light of analyses, as indicating a dual mechanism. The ether molecule is supposed to decompose in two ways:

(1) $C_2H_5OC_2H_5 = HCHO + CH_4 + C_2H_4$

$HCHO = H_2 + CO$

$C_2H_4 + H_2 = C_2H_6.$

(2) $C_2H_5OC_2H_5 = CH_3CHO + C_2H_6$

$CH_3CHO = CH_4 + CO.$

Analyses carried out at various stages during single runs indicate that the formation of acetaldehyde and ethane is favored at higher pressures. There would seem to be no *a priori* reason for expecting this. In any case it seems probable that the variation of the products with pressure is due to secondary reactions rather than to a change in the primary step, since the activation energy does not vary with pressure.

The products of the reaction

A comparison of the products obtained in the various investigations is given in Table II.

TABLE II. *The products of the reaction.*

Observer	Pressure, atm.	Temperature, °C	CO_2, %	C_2H_4, %	CO, %	CH_4, %	C_2H_6, %	H_2, %
Hinshelwood	ca. 0.3	477	0.0	8.9	27.9	54.4	8.8	—
Newitt & Vernon	0.26	530	—	7.4	30.8	47.9	8.7	4 1
Newitt & Vernon	2.95 to 13.8	490	0.1	0.8	31.4	32.2	31.1	2.1
Newitt & Vernon	2.95 to 13.8	490	0.1	1.9	30.6	33.3	31.6	1.4
Steacie and Solomon	26.9	426	0.1	5.0	26.5	33.3	32.6	—
Steacie and Solomon	34.4	424	0.1	4.0	30.3	32.3	31.5	—

It will be seen from the above table that the general nature of the products does not change with changing pressure. The main change on going from low to high pressure is an increase in the amount of ethane at the expense of ethylene and methane. It should be noted that virtually all the change occurs in going from 0.3 to 3 atmospheres; above this pressure the products remain virtually the same.

Homogeneity and pressure increase

A certain degree of difficulty arises in considering whether or not at high pressures we are dealing with the same reaction as at low pressures, and if, therefore, the data are comparable. We may rule out, on several grounds, the possibility of a concurrent heterogeneous reaction becoming prominent at high concentrations. Reaction vessels of two different sizes have been used and these have yielded identical results: The volume-surface ratio of Bomb *A* was 0.17 cc/cm², and of bomb *C* 0.04 cc/cm²: i.e., the volume surface ratio has been varied over fourfold. In any case, a high concentration in the gaseous phase tends to make any heterogeneous process negligible. In addition, the mere fact that the rates found are comparable with those of Newitt and Vernon at intermediate pressures would indicate that no additional complicating factor of this nature is involved.

A further point to be considered is the fact

[17] Kassel, *Kinetics of Homogeneous Gas Reactions*, New York, 1932.

[18] Rice and Sickmann, J. A. C. S. **54**, 3778 (1932). We are indebted to Dr. Rice for permitting us to see his complete results before their publication.

[19] Newitt and Vernon, Proc. Roy. Soc. **A135**, 307 (1932).

that as the initial pressure is increased the percentage pressure increase at completion decreases, thus:

Hinshelwood	low pressures	(210%)
	2.5 cm to 48.7 cm	188%
Newitt and Vernon	200 to 1200 cm	175%
Steacie and Solomon	2040 cm	158%
	2600 cm	161%
	6800 cm	132%
	9700 cm	120%

However, it is possible to correct for this by assuming that a definite fraction of the total pressure increase indicates the same fractional decomposition, and all rate constants reported here have been calculated on that basis. In any case, even if this assumption is in error, it cannot throw the results out by a factor of more than 1.5. In order to reduce the results of the various investigations to a common basis the data have been treated as follows:

(*a*) *This investigation.* The apparent rate constants, listed in Table I, have been corrected to the true constants by allowing for the pressure increase at completion. The values of T_{20} (the time for 20 percent completion) have been calculated from the rate constants by using the relationship $T_{20}=0.223/k$. The data are summarized in Table III. The second to last column

TABLE III. *Summary of results.*

Pressure, cm	$\frac{10^4}{P}$	$k\times10^4$ (apparent), sec.$^{-1}$	$k\times10^4$ (true) sec.$^{-1}$	Total % pressure increase	T_{20}, min.
2040	4.90	1.1	0.70	158	53.1
2600	3.85	2.7	1.7	161	21.8
3100	3.23	3.0	1.9	(156)	19.5
4650	2.15	3.9	2.7	(145)	13.7
6800	1.47	6.4	4.9	132	7.6
9700	1.03	6.7	5.6	120	6.6
12,700	0.79	6.7	6.0	(112)	6.2
14,500	0.69	6.9	6.4	(108)	5.8

in Table III gives the total pressure increase at completion; the values in brackets were obtained by interpolation or extrapolation.

(*b*) *Hinshelwood.* Hinshelwood's data for 525°C were used. The data are given in the form of times for a 50 percent pressure increase. We may assume with Hinshelwood that this represents 26.6 percent reaction. The values are then multiplied by 0.722 to give T_{20}. Using 53,000 calories for the energy of activation, we then multiply by 120.5 to obtain T_{20} at 426°C. It is true that the variation of rate with pressure will be slightly different at 426°C, but the error thus introduced is negligible.

(*c*) *Steacie.* Steacie's results at 478°C have been treated in the same way, again assuming that 188 percent pressure increase corresponds to complete reaction.

(*d*) *Rice and Sickman.* We have used Rice and Sickman's values at 478 and 462°C. Their results are given in the form of constants expressing the rate of pressure increase. These have been transformed as before assuming 188 percent increase at completion. In correcting to 426°C we have used 53,000 calories for the heat of activation instead of 60,000 as reported by them, in order to make the calculations of the various investigations consistent with one another.

(*e*) *Newitt and Vernon.* Results at 462 and 490°C have been used. The data have been recalculated on the basis of a pressure increase at completion of 175 percent as found by Newitt and Vernon.

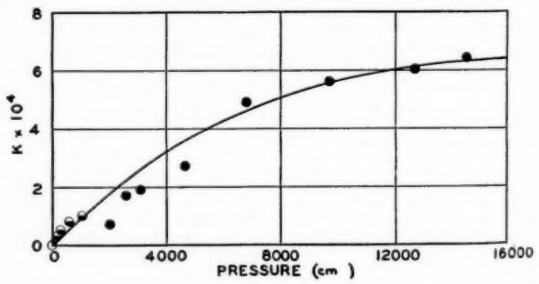


FIG. 7. Variation of rate constant with pressure. Black circles, Steacie and Solomon; black and white circles, Newitt and Vernon; open circles, Hinshelwood, Steacie, Kassel, Rice and Sickmann.

The data of all these investigations, recalculated as described above, are plotted in Figs. 7 and 8. It is evident, especially from Fig. 8, that it is absurd to extrapolate low pressure measurements in a linear fashion in order to obtain the rate at infinite pressure. Nevertheless even the proponents of theories II and III have had to resort to the simple Hinshelwood theory in obtaining k_∞ by a linear extrapolation of a $1/k-1/P$ plot. The value thus obtained with ethyl ether would indicate a rate about 50 times slower than that reported here at 14,500 cm.

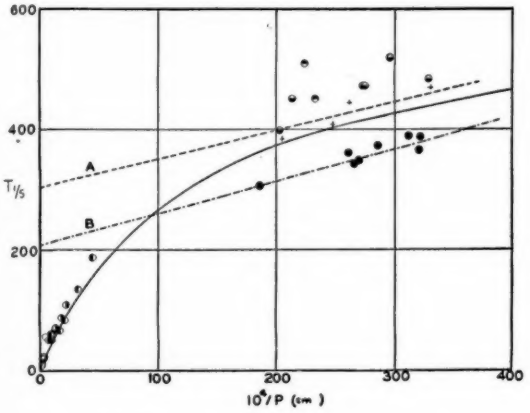


FIG. 8. $T_{1/5}-1/P$ plot. Circles, lower half black, Rice and Sickmann, 478°C; circles, upper half black, Rice and Sickmann, 462°C; crosses, Hinshelwood, 525°C; black circles, Steacie, 478°C; circles, right half black, Newitt and Vernon, 462°C; circles, left half black, Newitt and Vernon, 490°C; open circles, Steacie and Solomon, 426°C; *A*, Kassel's extrapolation of Hinshelwood's data; *B*, extrapolation of Steacie's data.

It is obvious that although a certain amount of error may be introduced into the high pressure results on account of aberrations from the ideal gas law such errors can have no effect on the general result that the rate is much higher at high pressures than would have been predicted. It is also possible that a concurrent bimolecular reaction might occur at low pressures, but not come into prominence until high pressures were attained. This would account for the high pressure rate being greater than that previously predicted, but such an explanation is ruled out by the fact that at very high pressures the rate constant is tending to become essentially independent of the pressure in the manner characteristic of unimolecular reactions.

DISCUSSION

Some interesting conclusions may be reached from a consideration of Fig. 7. The rate of reaction is still falling off at a pressure of 14,500 cm. If we assume that the rate would remain approximately constant at higher pressures, then as a rough approximation we may consider that at this pressure the rate of activation is just great enough to keep up the rate of reaction. We may therefore determine the number of squared terms involved.

At 699°K and 14,500 cm pressure the number of molecules reacting per cc per second is 1.16×10^{18}, assuming that the ideal gas law holds. This value may be in error by 10 or 15 percent on account of gas law aberrations, but this error is negligible compared to that introduced by the uncertainty in the collision number at high pressures. The total number of collisions per second is approximately given by

$$\sqrt{2}\pi s^2 n^2 (3RT/M)^{\frac{1}{2}}\cdot 1/(1-nb),$$

where s is the molecular diameter, n is the number of molecules per cc (2.02×10^{21}), and b is four times the volume of the molecule, which is assumed to be spherical.[20] Taking s as 5×10^{-8} cm, the number of collisions per cc per second is 1.41×10^{33}. On the basis of the Hinshelwood theory, taking E as 53,000 calories, we have

$$\frac{e^{-(53,000+(n/2-1)RT)/RT}\left[\dfrac{53,000+(n/2-1)RT}{RT}\right]^{n/2-1}}{\lfloor n/2-1}=\frac{1.16\times10^{18}}{1.41\times10^{33}}.$$

Whence we obtain

$$\frac{(38.29+n/2-1)^{n/2-1}}{e^{n/2-1}\lfloor n/2-1}=35.$$

If $n=4$ the left-hand side equals 14, if $n=6$ it is 109. It must be pointed out that Kistiakowsky[21] found that the collision formula correction factor, $1/(1-nb)$, failed at concentrations above 8500 cm. Above this pressure the number of collisions increases with great rapidity. This would tend to still further reduce the value of n. We are justified therefore in considering that the number of squared terms is not greater than 4.

Hinshelwood[2] has found in a similar manner that in order to account for the behavior of ethyl ether at ordinary pressures about 8 squared terms are necessary. We have now arrived at an apparent impasse: the observed rate at 20 cm cannot be accounted for unless n is greater than 8, but the fact that the rate is still falling off at 14,500 cm cannot be accounted for unless n is

[20] O. E. Meyer, *Kinetische Theorie der Gase*, Breslau (1899).

[21] Kistiakowsky, J. A. C. S. 50, 2315 (1928).

at least as small as 4. Also, the high pressure rate is much greater than would be expected on the basis of the application of theories II and III to the low pressure results.

The above calculation has been made on the basis of the simple Hinshelwood theory, and is of course only approximate. It would undoubtedly be more accurate to make a more elaborate calculation on the basis of theory II or III. Owing to the approximations involved, however, this would hardly be worth while. In any case the main point at issue would not be altered, namely, that any value of n which is consistent with the low pressure results is not applicable to those at high pressures, and *vice versa*.

The simplest assumption to make is that the number of degrees of freedom involved may be some function of the time between collisions. At very low pressures, where the time between collisions is comparatively large, eight squared terms are insufficient to maintain the rate and it falls off slowly as the pressure is decreased. At very high pressures, when the time between collisions is small, a much smaller value of n is required in order to maintain the rate. At still higher pressures, presumably, n will finally equal 2, the only vibrational degree of freedom involved being that in which the actual rupture of the molecule occurs. This would most probably be expected when the time between collisions is of the same order of magnitude as the time of vibration (10^{-13} to 10^{-14} sec.). The time between collisions at 14,500 cm is about 10^{-12} sec. (or possibly considerably smaller since the correction factor is becoming very uncertain). On this basis at very low pressures we would expect n to increase to a maximum until the number of degrees of freedom participating in the activation is given by the total number of oscillators in the molecule.

The mechanism for limiting the number of degrees of freedom would most probably be some form of atomic "insulators" suggested by O. K. Rice.[22] As the collision frequency increases less time is offered for the various degrees of freedom to come into play, and the insulators become more and more effective in limiting the critical energy to one oscillator.

In order to account for their results with acetaldehyde, Fletcher and Hinshelwood[7] found it necessary to postulate the existence, over various pressure ranges, of a number of activated states, each associated with its own transition probability. By assuming a change with pressure in the value of n, we arrive at the same result, i.e., the rate-pressure curve should be made up of a series of segments smoothly joined and corresponding to various values of n. However, since we are dealing with a large number of molecules constituting a statistical assemblage, we may expect that rather than sharp breaks in the curve as n changes, the curve will represent a continuous and progressive change in n. It is difficult to see how Fletcher and Hinshelwood can justify the clear-cut angles between the various segments of the rate-pressure curves, in view of the accuracy of the experimental data. It would be far more logical to expect a gradual transition from one activated state to another.

Since the completion of this work a paper has appeared by Hunter[23] on the decomposition of nitrous oxide up to pressures of 40 atmospheres. He finds that the rate increases considerably with increasing pressure, and interprets his results in the manner proposed by Fletcher and Hinshelwood. He finds that about 4 squared terms are required to account for the observed rate at 40 atmospheres. The rate is still increasing at this pressure, and on the theory outlined here it would seem likely that n is tending towards 2 at high pressures. (Hunter's calculations are probably considerably in error, since he neglects to correct the collision frequency for aberrations from the ideal gas law. Such a correction, however, would not change the general conclusions to be drawn from his work.)

Further work on the decomposition of ethyl ether is in progress. It is planned to (a) investigate the reaction at lower pressures by the same method so as to tie in with the low pressure results, (b) extend the work to still higher pressures, and (c) follow the rate by analysis at the higher pressures so as to eliminate effects due to gas law aberrations. Until such work is done we have thought it desirable to defer any discussion of the exact form of the pressure-rate curve over the entire pressure range.

[22] Rice, Zeits. f. physik. Chemie **B7**, 226 (1930).

[23] Hunter, Proc. Roy. Soc. **A144**, 386 (1934).

The Disposition of Work Energy Applied to Crystals*

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The experiments described in this paper were initiated for the purely practical purpose of securing data to be used for an energy balance of the process of comminution of solids. The technologic problem is not considered here but rather the antecedent fundamental and scientific one of attempting to describe the thermodynamic properties of crystals as a function of particle size. It has been customary to ascribe observable variations in the properties of crystalline materials of large or fine particle size to a change of free energy, entropy or heat content resultant from the subdivision. Consideration of the first law of thermodynamics with reference to the application of work energy to crystals allows for only two obvious possibilities: (1) The heat produced in the crystals by the applied work is equal to it, whence no change of intrinsic energy of the material can occur; or (2) part only of the work appears as heat and the intrinsic energy of the crystals must increase. In this latter case, it is supposed that the energy corresponding to the increase of intrinsic energy is "stored" in the surficial layers of the crystal particles. We shall offer no apology for approaching the problem of testing these alternatives in a strictly empirical manner and for presenting data which may seem to contradict much of previous theory and experiment concerning the "surface energy" of solids. However tempting a review and criticism of previous attempts to measure or theoretically define this quantity might be, the elementary approach represented by our work now seems essential for understanding of the anomalous results, both of ourselves and others. Experimental test based on the first law, as expressed above, obviously could be either by (1) attempting to determine the change of intrinsic energy of fine compared to coarse particles of suitable materials or (2) by comparing the work and heat during the comminution process. Both of these experimental alternatives are described below. Thus we shall first describe experiments upon the heat of solution of fine and coarse calcite, designed to reveal measurable differences of intrinsic energy due to comminution. Further, we have investigated the specific heat at low temperatures of similar samples of calcite, and later of finely drawn wires of copper and aluminum in the annealed compared to the cold-worked state, referring to that part of the intrinsic energy represented by heat content. Finally, in the case of copper and aluminum, we have adopted the second experimental alternative of comparing the work and heat during a drawing process.

PART I. HEATS OF SOLUTION OF FINE AND COARSE CALCITE

THE mineral calcite was chosen for a test of the change of intrinsic energy due to comminution for a number of excellent experimental reasons. Its heat of solution in hydrochloric acid is near 4000 calories per formula weight and Bäckström[1] had reported a difference of 60 calories per f.w. between large crystals and a sample ground to 10-micron size. Such a quantity should be easily detectable, even with only fair calorimetric precision, in comparison with the total of 4000. The rapid and easy solution in acid, the high purity obtainable in natural crystals and the ease of precise analysis commend this choice further.

Experimental work

The calorimetric method used to determine the heat of solution of calcite samples of varying fineness has been described previously by one of us[2] in connection with the heat of solution of zinc oxide and no essential change of method or accuracy was made in the present experiments. The limiting sensitivity of the calorimeter is approximately 1 calorie.

The rate of dissolution of calcite, in very fine sizes, was so great that excessive foaming ordinarily took place. This difficulty was easily

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[1] Bäckström, J. Am. Chem. Soc. **47**, 2438 (1925).

[2] Maier, J. Am. Chem. Soc. **52**, 2159 (1930).

remedied by tying several thicknesses of surgical gauze about the thin walled flask used for the calcite container. This flask was broken inside the gauze bag so formed at the appropriate instant. The first evolution of gas after breakage of the flask distends the bag and prevents further ingress of acid until the carbon dioxide has escaped. The dissolution of calcite proceeds smoothly by successive distentions, and is complete for the finest sizes in about 4 minutes from the instant of breaking. By using a smaller or greater number of layers of gauze, it was possible to bring the total time of dissolving to within practically identical limits for sizes from $\frac{1}{4}$ inch to 0.5 micron, thus insuring the greatest degree of comparableness in the necessary calorimetric corrections.

Materials. The hydrochloric acid used for dissolution of the calcite was of C. P. grade, without further purification. It was diluted to a concentration of $1HCl : 20H_2O$. Analysis by gravimetric means showed the actual HCl content to be 9.192 percent and the theoretical HCl content 9.191 percent. Before use, this acid was saturated with CO_2 at 23–24°C, by using gas which had been saturated with water vapor above an identical HCl solution.

Well-developed calcite crystals were selected and prepared in three sizes. Two coarser sizes, prepared by simple crushing were $-4+6$, and $-200+270$ mesh, separated by standard screens. A third sample was prepared by grinding in a mechanical agate mortar, with frequent classification by means of an air elutriator, arranged as described by Roller.[3] The particle size of the final product was fairly uniform and determined by microscopic means to average near 0.5 micron. The minimum visible size was greater than 0.1 micron and the maximum near 1 micron but there were relatively few particles of limiting sizes.

The finest size calcite had a very low apparent density, and to secure sufficient compactness so that an adequate amount could be put into our calorimetric containers and to improve the thermal conductivity of the material, it was compressed into pellets. A pressure of about 2 tons per sq. in. was used in the press, resulting in fairly dense pellets, which were again pulverized to a size approximating 14–35 mesh.

Experimental procedure. Samples of 50.0375 grams (vacuum basis), or $\frac{1}{2}$ formula weight, were sealed, after careful drying at 105°C, into thin-bottomed flasks, as described in the previous reference. The weight of hydrochloric acid used was 595.19 grams, corresponding to $1.5HCl : 30H_2O$, without, however, any attempt to correct for dissolved CO_2, which is small in this strength acid. Calorimetric determinations were: (1) Determination of the initial heat capacity of the calorimeter by direct electrical methods, under such conditions that the final temperature was near 24.6°C. About 7000 calories of heat were generated by the accurately calibrated manganin heater. (2) When thermal equilibrium had been attained the flask was broken and a conventional determination carried out. The attempt was made to finish near 25°C. (3) After this latter test the heat capacity was determined again over the range from 25–26$\frac{1}{3}$°C by repetition of (1).

Calculation of results. The method of calculation of results has been described in the previous paper but it may be repeated here that the temperature coefficient of the reaction, ΔC_p, is directly determined by the difference between the heat contents measured under (3) and (1) and that the constancy of this quantity is an excellent check upon satisfactory operation of the calorimeter. Systematic errors are referable to the energy determinations. Recalibration of the standard cells and resistances used imply no error here greater than 1 part per 100,000.

In converting international joules to 15° calories, the factor 1/4.184 was used. The final figure of the resistance thermometer reading has been dropped in each case, except as mentioned hereinafter.

The chief source of uncertainty is in correction of the temperature rise. The calorimeter comes to thermal equilibrium in 5 to 8 minutes so that calculation by a graphic Regnault-Pfaundler method is eminently satisfactory but the heat exchange with the surroundings is erratic to about 1 percent near the adiabatic point, probably due to the well-known adsorbed film effect on the gold-plated calorimeter shell. The known uncertainty due to this cause is approximately 5 calories; for this reason, no greater

[3] Roller, U. S. Bur. Mines Tech. Paper 490 (1931).

TABLE I. *Heat of solution of $0.5CaCO_3$ in $1.5HCl : 30H_2O$.*

Exp. No.	Aver. part. size, mm	Initial heat capacity	Final heat capacity	ΔC_p	Temp. rise, °C ΔT	Cooling rate correction	Corrected temp. rise, °C	Final temp., °C	ΔH_T $\frac{1}{2}CaCO_3$	ΔH_{298} $\frac{1}{2}CaCO_3$	Mean ΔH_{298} per $CaCO_3$	A. D. of M.
1	4.0	5671.0	5697.9	26.9	0.3603	−0.0135	0.3468	24.62	−1966.7	−1953.6		
2	4.0	5681.2	5709.6	28.4	0.3465	−0.0017	0.3448	25.04	−1958.9	−1960.3	− 3913.8	±4.6
7	4.0	5670.5	5702.1	32.4	0.3498	−0.0038	0.3460	24.85	−1962.0	−1956.8		
3	0.065	5695.5	5723.6	28.1	0.3406	+0.0021	0.3427	25.22	−1951.8	−1959.4		
4	0.065	5671.5	5701.9	30.4	0.3471	−0.0015	0.3456	25.01	−1954.4	−1954.7	− 3912.8	±4.0
8	0.065	5723.7	5748.8	25.1	0.3425	−0.0008	0.3417	24.98	−1955.8	−1955.1		
5	0.0005	5700.7	5726.5	25.8	0.3673	−0.0030	0.3643	24.80	−2075.6	−2068.7	−(4132.4)	
6	0.0005	5656.9	5685.0	28.1	0.3715	−0.0042	0.3673	24.60	−2077.8	−2064.0		

relative precision than 10 calories per formula weight is claimed for these experiments. The absolute accuracy may be no better than several times this amount, due rather to such factors as imperfect saturation of evolved gases by water vapor, ununiformity due to the very rapid completion of the reaction and other secondary effects, rather than to the calorimeter characteristics.

Experimental results. The results of eight determinations of heat of solution of three sizes of calcite are presented in Table I, the order of measurement being the sequence of experiment numbers.

In correcting the results of these experiments to a final temperature of 25°C the observed value of ΔC_p, averaging 28 calories, has been increased by 4.5 calories to represent the heat content of $\frac{1}{2}CO_2$ lost by the system. No corrections for heat of vaporization of water with the CO_2 or for external work done by the CO_2 in its escape have been made. The chief interest is in comparison of results for varying degrees of fineness.

At first glance, the results of Table I would indicate that Bächström's result of an increased heat of solution of 60 calories per f.w. for 10-micron size material was approximately confirmed by the figures for 0.065- and 0.0005-mm sizes, showing an apparent increase of 4132.4 $-3912.8 = 219.6$ cal/f.w. for this range.

Had our experimental work ceased at this point, publication of our results would have burdened chemical literature with still one more erroneous figure for "surface energy," although the result would no doubt have been conventionally acceptable, if unremarkable, as falling in with previous determinations. In this case, however, we were fortunately constrained to make precise analyses of the materials used. Reference to previous attempts at determination of the energy differences of fine and coarse materials shows them to be singularly free from this elementary precaution.

Analyses of materials

The thermal decomposition of calcite at 1000°C in a slow stream of pure, dry nitrogen was found to be a precise method of analysis for these relatively pure samples, with the use of a conventional combustion train. Water and carbon dioxide evolved were weighed after collection by fresh calcium chloride and ascarite and their sum was compared with the loss in weight of sample. By using a clear silica-glass tube and careful preliminary drying, the combined H_2O and CO_2 checked the loss in weight of a 4-gram sample to within 0.2 milligram in all cases.

Analysis of the sample crushed to 0.065 mm showed a CO_2 content of 43.973 percent, without correcting weights to a vacuum basis. An approximate correction to vacuum would indicate 43.959 percent CO_2. Based on the atomic weights 40.07 for calcium and 12.005 for carbon, the theoretical CO_2 content of calcite is 43.972 percent and the purity of this sample was at least 99.970 percent.

In the case of the 0.5-micron size, calculation from the CO_2 content showed only 98.656 percent $CaCO_3$. Since the weight of CO_2 and water found by analysis checked the loss in weight of the

calcite during decomposition to within 0.2 milligram, the composition of the impurity may be calculated on the assumption that it consisted only of $Ca(OH)_2$ and H_2O, the actual figures being 0.726 percent $Ca(OH)_2$ and 0.618 percent H_2O. No silica (from the mortar used in grinding) could be detected in this sample.

It is apparent that this percentage of $Ca(OH)_2$ would produce serious error in the heat-of-solution tests 5 and 6, of Table I. The most recent measurements of the heats of solution of $Ca(OH)_2$ in hydrochloric acid have been made by Thorvaldson and Brown[4] who used acid of concentration 1:200 and obtained as best value 30,850 $cal._{20°}$, at 20°C, per formula weight. In the present work it was thought necessary to repeat the determination of the heat of solution of $Ca(OH)_2$, by using the concentrations of HCl and $CaCl_2$ as obtained after dissolution of $\frac{1}{2}CaCO_3$ in $1.5HCl : 30H_2O$, thus representing approximately identical final conditions and eliminating heat-of-dilution effects as much as possible. For this purpose, the solutions obtained in experiments 7 and 8 of Table I were again placed in the calorimeter and the heat of solution of two samples of slightly less than 1 gram each of CaO, which had been hydrated with the same proportion of water as corresponded to the 0.5-micron sample analysis, was determined.

The samples of CaO used were from the previous analysis of calcite and undoubtedly were of high purity. In these determinations of heat of solution, the last figure of the resistance thermometer reading was retained (because of the low temperature rise involved). The data themselves are shown in Table II.

The final result for $Ca(OH)_2$ shown in Table II indicates that the heats of dilution involved in comparison with the result of Thorvaldson and Brown are substantially negligible in this case. By using the figure 413.9 calories per gram, corresponding to $\Delta H = -30{,}670$, the results of experiments on the 0.5-micron calcite of Table I may be corrected as follows: 100.075 grams evolve 4132.4 calories but contain 98.730 grams $CaCO_3$ and 0.7264 gram $Ca(OH)_2$; but $0.7264 \times 413.9 = 300.7$ calories evolved due to the hydroxide; the net, $4132.4 - 300.7 = 3831.7$ corresponds to $3831.7 \times 100.075/98.730 = 3883.4$ calories per $CaCO_3$, corrected. This figure is 29.4 calories *less* than for the 0.065 mm material.[5] The correction for impurities known to be present in the 0.5-micron size more than accounts for the difference observed.

TABLE II. *Heat of solution of $Ca(OH)_2$ in $\frac{1}{2}HCl : 1CaCl_2 : 30H_2O$.*

	Experiment 1	Experiment 2
Weight CaO used, grams	0.9270	0.9418
Heat capacity of calorimeter, calories	5689.0	5658.0
Temperature rise, °C, uncorrected	0.08116	0.09249
Cooling-rate correction	+0.00812	−0.00159
Corrected ΔT, °C	0.08928	0.09090
Final temperature, °C	25.16	25.03
Heat of solution, per gram $Ca(OH)_2$, calories	414.6	413.2
ΔH per $Ca(OH)_2$, average, calories	−30670	15°

PART II. ENTROPY CHANGE DUE TO COMMINUTION

Fine and coarse calcite

Specific-heat determinations were made by Anderson on the original sample of calcite crushed to 0.75 mm average size and compared with similar determinations on the 0.5-micron size as used above. These results have been published.[6]

After correction for the impurities in the fine calcite it was found that the two sets of data were experimentally identical in the lower temperature ranges (50 to 150°K) but that the fine material showed a slight progressive increase of specific heat compared to coarse above this range. Near ordinary temperatures this difference became slightly less than 1 percent as a maximum. Had the difference persisted to low temperatures the conclusion that a real difference

[4] Thorvaldson and Brown, J. Am. Chem. Soc. **52**, 80 (1930).

[5] If appropriate corrections for external work and heat of vaporization of water above the solutions used are made and the differences in quantity of CO_2 evolved taken into account, this discrepancy becomes 28.9 calories in the same direction. The reason for the overcorrection is discussed in more detail in connection with density determinations below.

[6] Anderson, J. Am. Chem. Soc. **56**, 340 (1934).

of heat content existed might have been warranted but it is known that the maximum errors in calorimetric work of this sort appear near ordinary temperatures and have been shown by other work to lie near 2 percent as a maximum, with an average uncertainty of about 1 percent. The differences observed in this case were, then, only as great as the supposed experimental error and the results are inconclusive as far as calcite is concerned. The differences observed in the higher temperature ranges certainly were no greater than those naturally ascribable to the effect of the poor heat conductivity of the fine material, even after its compression to granules.

Work upon metallic wires

The factors causing rather high calorimetric errors of specific-heat determinations in the method used for measuring this quantity at low temperatures are minimized considerably when metallic samples are in question. Not only is the mass of sample carried by a given calorimeter much greater, but more important is the fact that high thermal conductivity greatly reduces the necessary calorimetric corrections constituting the chief source of error of this method. We therefore decided again to attempt to observe possible entropy differences in samples of cold-worked as compared to annealed metals.

The fundamental difference in the nature of the comminution process when carried out upon calcite, or by drawing wires, is obviously that the first produces new external crystal surfaces, whereas the second process may produce new internal crystal surfaces. It will be more suitable to postpone more searching inquiry into the differences and analogies in the two cases until all the experimental evidence has been adduced.

Experimental

The calorimeter used to determine the specific heats at low temperatures has been previously described by one of us.[7] The sample of copper wire was specially prepared for us of deoxidized metal through the courtesy of the Bell Telephone Laboratories, who furnished it to us in the form of hard-drawn wire. It had been drawn from 0.180 to 0.010 inch without annealing and in such a way as to insure every precaution against self-annealing. It was further drawn by us to 0.0075 inch, and the final wire was cut into small pieces approximately 0.010 inch long. Enough quantity was prepared for two calorimeter samples, one of which was annealed at 400°C for 16 hours in a high vacuum.

The aluminum was of high purity (99.985 percent) and was drawn from No. 16 B & S to about No. 32 B & S gauge in a manner similar to the copper. The annealed sample was heated in a high vacuum at 460°C for 18 hours.

The samples used for specific-heat measurements were of the following masses: Hard-drawn copper, 595.1 grams; annealed copper, 603.9 grams; hard-drawn aluminum, 180.5 grams; annealed aluminum, 175.2 grams. The experimental results are shown in Tables III to VI, where the specific-heat values are given in 15° calories, with 4.184 as the conversion factor, joules to calories.

To compare the results of the measurements on the hard-drawn with the annealed samples, each of the authors has independently plotted the original experimental points, drawn suitable smooth curves through them and compared interpolated common temperature results as read

TABLE III. *Specific heat of hard-drawn copper at low temperatures.*

T°K	C_p per g-atom	T°K	C_p per g-atom
54.14	1.734	153.5	5.031
56.72	1.853	190.3	5.314
60.18	2.102	213.4	5.508
69.63	2.619	240.4	5.636
83.23	3.198	261.0	5.718
101.5	3.886	279.3	5.772
126.3	4.509	294.3	5.829

TABLE IV. *Specific heat of annealed copper at low temperatures.*

T°K	C_p per g-atom	T°K	C_p per g-atom
53.29	1.728	152.8	4.952
57.72	1.952	188.2	5.281
60.56	2.127	209.6	5.481
72.29	2.732	241.7	5.644
84.19	3.210	267.5	5.749
99.20	3.809	288.1	5.792
123.1	4.444	291.9	5.805
		293.0	5.802

[7] Anderson, J. Am. Chem. Soc. **52**, 2296, 2712 (1930).

TABLE V. *Specific heat of hard-drawn aluminum at low temperatures.*

T°K	C_p per g-atom	T°K	C_p per g-atom
56.18	1.177	126.5	3.886
59.60	1.368	141.7	4.247
63.86	1.562	163.4	4.637
75.44	2.092	185.0	4.913
79.99	2.296	200.4	5.105
84.45	2.483	219.6	5.298
90.24	2.722	241.1	5.452
92.85	2.810	257.4	5.537
100.6	3.104	272.8	5.633
112.5	3.494	290.6	5.729

TABLE VI. *Specific heat of annealed aluminum at low temperatures.*

T°K	C_p per g-atom	T°K	C_p per g-atom
54.80	1.129	164.2	4.647
58.42	1.289	186.2	4.932
61.84	1.472	199.4	5.100
69.99	1.856	218.9	5.307
83.96	2.457	243.8	5.486
97.68	2.994	257.5	5.558
112.4	3.533	278.9	5.698
124.6	3.849	296.3	5.741
141.0	4.239		

from these curves. Thus it was found that the mean algebraic difference between hard-drawn and annealed copper was −0.001 calorie/degree/gram-atom, with an average deviation of the mean ignoring the algebraic sign of the difference of 0.011. In the case of aluminum the mean algebraic difference was −0.006, with an average deviation of 0.009 from the mean.

Further, low temperature specific-heat measurements recently have been made in the University of California laboratories, under the direction of Professor Giauque, of single crystals of copper and aluminum; we have compared our results with these at the same temperatures as in comparing differences, with the use of Meads' interpolation of his own data.[8] To complete the picture, we have further calculated the average deviation of the points experimentally determined from the smoothed curves drawn for our own results. All these figures are summarized in Table VII.

TABLE VII. *Average deviations of specific heats 50–290°K calorie/degree/gram-atom.*

Material	Form	Average deviation of orig. determinations from smoothed curve	Average differences of C_p between points at 13 interpolated temperatures, 50° to 290°K
Copper	Single crystal		+0.020
	Hard-drawn	0.009	
			− .011
	Annealed	.016	
Aluminum	Single crystal		+ .034
	Hard-drawn	.006	
			− .009
	Annealed	.010	

These comparisons leave no question as to the absence of detectable effect on heat content as *directly measurable* entropy due to the cold working of copper and aluminum, since the differences observed between cold-worked and annealed samples are of the same magnitude as the uncertainty of the original measurements. Furthermore, it is noted that the differences between our results and Meads' for single crystals are of the opposite sign from those expected if cold working increased the "randomness" of the metal atoms, in that the single crystal had slightly higher heat contents at the same temperature.

We shall not discuss here the considerable number of references in the literature purporting to show the effect of mechanical working upon the specific heat of metals but shall only refer to the fact that our results confirm those of Eucken and Werth[9] on copper and shall point out further that the relative accuracy of the measurements reported above is on the average better than 0.2 percent. In comparing our results with those of Meads' on single crystals, the specific-heat values near liquid-air temperatures are practically identical and only in the higher temperature ranges does an average difference of about ½ percent occur. This laboratory is on the same temperature scale as that of Professor Giauque but a slight difference in method of applying

[8] Meads, P. F., Ph.D. Thesis, University of California, 1932.

[9] A. Eucken, and H. Werth, Zeits. anorg. Chemie **188**, 152 (1930).

temperature gradient and cooling-rate corrections in the two laboratories is probably sufficient to account for the differences observed in the upper ranges of the experimental measurements.

Part III. Comparison of Work and Heat in a Wire-Drawing Process

It seems obvious from the above that if any difference of entropy exists in pure metals resulting from crystal size or mechanical work it is not detectable with the precision of measurements now obtainable and if it exists at all must come in as "zero-point" difference. Aside from this, it was apparent that even if the entropy change were strictly zero in going from single crystals to annealed or cold-worked wires, a change of heat content still might be entirely ascribable to a change of free energy. Further, it is experimentally impracticable to determine the possible difference of heat content of such a metal as aluminum in various conditions by heat-of-solution experiments. If a gram-atom is dissolved in HCl, some 127,000 calories are evolved, in which the experimental problem of finding the looked-for quantities of perhaps less than 100 calories difference would be nearly insuperable. In a wire-drawing process, however, a drawing tension just below the ultimate strength of a No. 18 gauge wire requires work to be done at a rate of approximately 200–300 calories per gram-atom. Comparison of heat and work in such a process then offers the best possible chance of determining possible changes of heat content of a few calories magnitude, which may be associated with the severest possible cold working.

Experimental arrangements

To carry out the necessary measurements for comparing work and heat in a wire-drawing process the calorimeter used for the calcite-dissolution experiments was so modified that a bobbin of wire and die could be submerged in it and a special device was arranged for measuring the tension of the wire continuously as it was being withdrawn from the calorimeter; the resulting product of length of wire and tension furnished the required work quantity for comparison with the heat shown by the calorimeter.

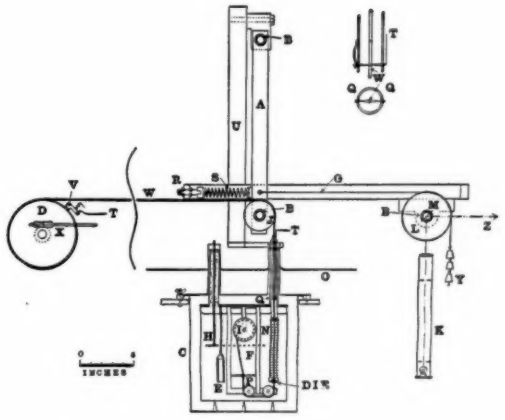

Fig. 1. Diagram of apparatus for comparing work and heat in wire drawing.

The arrangement is shown more or less schematically in Fig. 1. In calorimeter C the reciprocating stirrer H and the resistance thermometer E are unchanged, compared with the previously described reference. Frame F, of light-weight but fairly rigid brass angles, carries the bobbin I, containing the sample of wire to be drawn, and pulleys P, which serve to carry wire to the die, which is externally supported through one of the calorimeter chimneys by the structure N. The upper half of N is a thin-walled Bakelite tube, whose upper end is clamped firmly to external upright U, which also serves to support the tension meter. The lower half of N consists of a series of thin copper washers mounted on $\frac{1}{16}$ inch drill-steel rods with a driving fit. This construction serves the twofold purpose of stiffening the supporting members for the die socket while still permitting free access of calorimeter fluid to the wire and further increasing the thermal conductivity of that part of the calorimeter near the wire which is just through the die.

Even with the precautionary measures taken to assure transmittal of residual heat from the drawn wire to the calorimeter by means of N, it was found, after a few experiments had been performed, that the wire during drawing emerged from the bath several tenths of a degree above the calorimeter temperature. A loop thermocouple was then installed at Q, an enlarged section being shown at $Q-Q$. The wire drawn passes through a crossed loop of No. 36 constantan

wire held in slight tension by a small spring and the sliding contact, which is nearly frictionless, constitutes the hot junction of a thermel. Constantan lead T of $Q-Q$ goes to a cold junction in ice and the other lead is carried through the wire, being drawn as described later.

The tension-measuring device consists of pendulum-like arm A suspended near its upper end from the rigid member U and carrying a nearly frictionless sheave J at its lower end. There are ball bearings B at each end and wire W makes a right-angle turn over sheave J. Upright member U also carries a cross-member R serving to support an adjustable spring S, opposed to which is a fine-tension piano-steel wire G. G makes several turns over the nearly frictionless and well-balanced wheel L, which carries mirror M mounted on its shaft, the whole being held taut by weights Y. A beam of light from slit projector K is reflected by the mirror to a scale several meters farther along Z.

Arm A is free to swing through a small arc about its upper ball bearing. Weights Y are adjusted to correspond to about 90 percent of the tension in wire W, the remainder of the tension being taken up by the spring S. With this device a sensitivity of about 3 grams was obtained when an ordinary automobile valve spring at S and an optical beam of about 3 meters were used. Since the total tension was usually near 5000 grams the sensitivity was near 0.05 percent but the accuracy naturally was somewhat worse than this because of fluctuations of tension when the drawing was in progress.

After leaving the tension meter the wire was wound upon the accurately turned steel drum D which was rotated at a constant predetermined speed by worm drive X. A revolution counter and indicator, not shown in the drawing, recorded the revolutions of D from which the length of wire was calculated from the accurately measured diameters of drum and wire. The accuracy of determinations of wire length by this method was checked several times by actual measurement of wire on the drum and found to be within 0.1 percent.

A contactor, V, carried off the thermel lead corresponding to the couple whose hot junction was at Q. This contactor and its electrical connection T were of the identical metal as the wire, that is, aluminum when aluminum wire was drawn and copper for the copper-wire experiments. Lead T was carried to the ice bath for the cold junction connection.

Oil thermostat O, in which the calorimeter jacket was submerged, was maintained at a constant temperature near 25°C, with a variation of not more than 0.002° throughout the experiment.

The question of calorimetric fluid, which had also to serve as a lubricant for the die, was very troublesome at the beginning of the experiments. A light lubricating oil was found to have such low thermal conductivity and low fluidity that a lag of 20 minutes was observed in reaching thermal equilibrium. Kerosene was next tried and found to have a thermal lag of only 3 minutes but the die was not lubricated and the wire badly cut in drawing. Without efficient lubrication the tension meter fluctuated violently. Several experiments were performed with the wire on bobbin I coated with beeswax and with the use of a saturated solution of beeswax in kerosene as the calorimetric fluid. This adequately lubricated the die and had a low initial thermal lag but gave rise to secondary thermal effects, after a drawing experiment was concluded which were finally shown to be due to slow saturation of the kerosene with beeswax. Because the temperature coefficient of solubility of beeswax in kerosene is enormous a temperature rise of only a few tenths of a degree caused anomalies of 50 calories or more. We finally used kerosene containing as lubricant 10 percent of a soluble sulphurized lubricant, such as is used commercially for lubricating screw-cutting dies in automatic machinery. This liquid had adequate lubricating qualities and a thermal lag of only about 4 minutes and was free from detectable thermal after-effects. It had, however, a rather high coefficient of change of specific heat with temperature (2 percent per degree), which necessitated a correction in calculating results.

Experimental procedure—calorimetric

The heat capacity of calorimeter and contents was determined before and after each wire-drawing experiment. An accurately calibrated manganin heater (not shown in the drawing) was used for this purpose and current was

measured with a White double potentiometer and timed with a calibrated stop watch. Resistance, e.m.f., and time standards were checked at appropriate intervals to insure no systematic error. The heating current was adjusted to simulate the normal temperature rise during the drawing process, with a total temperature rise of about 0.3° which was measurable by the resistance thermometer used to a relative accuracy of about 0.0002°. The mean temperature of the initial heat-capacity determination was near 24.5°C and of the final near 25.5°C.

The actual measurement of heat developed usually occupied about 2 hours, the temperature rising from near 24.7 to approximately 25.0°. In calculation of the heat evolved the heat capacity of the calorimeter was corrected for one-half of the heat content of the wire withdrawn and to the mean temperature during the drawing process.

Tension measurements. Weights Y were so adjusted during each experiment that a deflection of 20 cm of the light spot opposite Z was secured. This usually allowed for any slight variation in the tension without going off scale. The position of the spot was read every minute during the drawing time. Since calibration of the tension meter showed almost exactly a linear relationship between tension and deflection, the simple average of these readings was taken as representing the work-tension.

Calibration of the tension meter was repeated after every experiment. It consisted of replacing wire W with a fine piano-steel wire similar to G but fastened at the normal die position. A ball-bearing pulley was substituted for drum D, care being taken that its top tangent was aligned accurately with the normal position of W and a system of weights of known mass, similar to Y, suspended from it to give the same position of the light spot as the average during the draw.

Length of wire. Drum D and the wire were measured with good micrometer calipers and the length of wire was calculated upon the assumption that the length was the number of turns times the circumference of a circle, with diameter equal to the sum of the drum plus 1 wire thickness. This was found to check closely with a number of actual measurements of wire removed from the drum.

Corrections. As has been stated, it was found that the wire leaving the calorimeter, even with the slow rate of withdrawal of 25 meters per hour, was several tenths of a degree above the bath temperature. The constantan-aluminum or constantan-copper thermel at Q reached a steady state intermediate between calorimeter bath and outside temperature before drawing, under static conditions. When the drawing started, the temperature at Q rose for some 8 to 10 minutes, then showed only a slight change corresponding to the drift of the calorimeter or surrounding temperatures. It was substantially at a steady state. It was assumed that this temperature increase represented the true excess of heat of the wire with respect to the bath. The motion of the wire obviously was so slow as not to affect appreciably the heat flow in the vertical section of wire which controlled the actual temperature at Q. The product of this temperature rise by the specific heat of the wire actually withdrawn, as determined by the average of readings taken every 10 minutes during an experiment, was added to the calorimetric heat.

Tension-meter corrections. As the wire passes over sheave J of the tension meter it is stretched by the curvature and at the same time a certain amount of work is done external to the calorimeter which must be accounted for. The observed length of wire on the drum was then correctable by the stretch and the observed tension under static conditions by the equivalent friction at J. The actual friction of J was negligible, the apparent friction being due to bending the wire about the curvature.

These two corrections were evaluated for aluminum and copper wires by removing arm A and using sheave J as the pulley of an Atwoods machine in the usual way. The elongation and equivalent friction were found to be a function of the tension but nearly independent of the speed at which the wire passed over J. The results of such a calibration for each metal are given in Table VIII. The accuracy of the elongation determinations was about 2 percent and of the equivalent friction about 5 percent, the chief source of inaccuracy being the change of dimensions and properties of the metal during each pass over the sheave. Since the elongation correction is itself about 1 percent of the total

TABLE VIII. *Corrections for tension meter, for wire 0.0370 inch diam., 2-inch sheave.*

Measured tension, kg	Aluminum Elongation, percent per pass	Aluminum Apparent friction, kg	Copper Elongation, percent per pass	Copper Apparent friction, kg
3.0	0.615	0.114	0.300	0.169
4.0	0.982	0.120	0.392	0.176
5.0	1.465	0.132	0.488	0.186
6.0	2.295	0.212	0.590	0.201
7.0	3.45	0.320	0.715	0.218
8.0	(beyond ultimate strength)		0.855	0.243
9.0			1.060	0.282
10.0			1.395	0.354
11.0			1.980	0.489

length and the friction correction about 2 to 3 percent of the total tension the errors involved in the determinations of the corrections clearly are negligible compared with the totals involved.

Experimental results

In Tables IX and X the final results of the comparisons of work and heat in the drawing of aluminum and copper, respectively, are recorded. Details of calorimetric data and of the various items of correction mentioned above are not shown since details of procedure and accuracy involved by them have been discussed above.

The first four experiments of Table IX were made with beeswax as lubricant and, as previously explained, the thermal after-effects caused by this render these results somewhat erratic. The correction for sensible heat removed by the wire was not applied until after experiment 3, at which time the slip-thermel was introduced into the apparatus. The magnitude of the corrections introducible in the first three experiments, judged by the succeeding experiments, would be from 10 to 20 calories additional to the heat item.

In experiments 5 to 8 the wire used, stated by the manufacturer to be soft drawn, was not re-annealed after winding upon bobbin *I*. Probably the result of experiment 5 should be rejected in the average of these tests, but application of Chauvenet's criterion hardly seemed justifiable. At any rate, the average discrepancy between work and heat is less than the average deviation of the mean of the results and it must be concluded that no evidence of energy "storage" is disclosed by these tests, the accuracy probably being in the neighborhood of 1.0 percent; in other words, on the average at least 99 percent of the work energy appeared as heat.

It was suspected, however, that even if the original wire were truly soft drawn merely

TABLE IX. *Comparison of work and heat in drawing aluminum.*

Exp. No.	Lubricant	Condition of wire	Correction for heat of wire withdrawn	Corrected tension, kg	Corrected length, meters	Work, cal.	Heat, cal.	Discrepancy, $W-H$	Discrepancy per g-at. Al
1	BW	S.D.	U	4.494	53.00	557.6	512.6	+45.0	+12.4
2	BW	S.D.	U	6.434	43.93	661.9	665.8	− 3.9	− 1.3
3	BW(s)	S.D.	U	5.403	54.66	691.5	655.0	36.5	+ 9.6
4	BW(s)	S.D.	C	4.210	54.36	535.7	530.1	+ 5.6	+ 1.5
5	Sol	S.D.	C	5.496	51.50	663.0	644.5	+18.5	+ 5.2
6	Sol	S.D.	C	4.615	51.86	560.4	565.4	− 5.0	− 1.4
7	Sol	S.D.	C	5.161	52.37	632.9	638.9	− 6.0	− 1.7
8	Sol	S.D.	C	4.335	48.86	496.0	490.4	+ 5.6	+ 1.7
								Average 5–8 =	+ 0.9±2.5
9	Sol	RA	C	4.580	51.87	556.3	537.1	+19.2	+ 5.4
10	Sol	RA	C	5.335	51.26	640.4	623.1	+17.3	+ 4.9
11	Sol	RA	C	5.305	51.27	636.9	628.9	+ 8.0	+ 2.3
12	Sol	RA	C	5.578	49.41	645.4	631.9	+13.5	+ 3.9
								Average 9–12 =	+ 4.1±1.0

BW, wire coated with beeswax; BW(s), wire coated with beeswax used in sat. sol. beeswax in kerosene; Sol, kerosene +10 percent sulphurized oil; S.D., soft drawn; RA, re-annealed; U, uncorrected; C, corrected.

TABLE X. *Comparison of work and heat in drawing copper.*

Exp. No.	Corrected tension, kg	Corrected length, meters	Work, cal.	Heat, cal.	Discrepancy, $W-H$	Discrepancy, per/g-at. Cu	Remarks
1	10.724	46.69	1172.4	1096.7	75.7	16.1	Wire A
2	5.054	48.18	570.2	498.1	72.1	15.2	Wire A, die-polished
3	4.866	48.40	574.8	513.8	61.0	12.8	Wire A
4	3.392	48.61	386.2	362.6	23.6	(5.0)	Wire A, wire-polished
5	6.014	35.92	505.9	453.3	52.6	14.8	Wire A
6	7.722	49.76	899.7	825.6	74.1	15.0	Wire B } Best results
7	6.608	49.49	765.7	694.5	71.2	14.6	Wire B }
						Average omitting (4)	14.8 ± 0.7

winding it on bobbin *I* would entail sufficient cold working to cause an element of uncertainty in these results. In the four succeeding experiments, 9 to 12, the wire, after being wound upon the bobbin, was annealed carefully in a high vacuum at 350–400°C for 12 hours. In these tests, which are the best of those on aluminum, more concordant results were obtained and we believe that the discrepancy between work and heat of 4.1 calories per gram-atom is real. This figure corresponds to the statement that approximately 98 percent of the work energy appears as heat.

In the experiments on copper, the results of which are shown in Table X, tests 1 to 4 suffered somewhat from rather sharp fluctuations of the tension required for drawing. All the samples in Table X were wire which had been annealed on the bobbin at 350–400°C for 12 hours and it was shown that the fluctuations were due to unevenness of the wire and burring at the die. Various expedients of polishing the die or wire were tried and these resulted in the considerable variations of drawing tension shown. Tests 5 to 7 were made on wires carefully drawn by ourselves before winding upon the bobbin and constitute the best results obtained.

In this case there can be no doubt as to the reality of a discrepancy between work and heat which averages 14.8 calories per gram-atom, so that approximately 90 percent of the work appears as heat. The results show that the discrepancy is a function of the mass of wire and, by noting the effect of tension, it seems clear that it is also practically independent of the tension, provided it exceeds a certain rather indefinite minimum of about 5 kilograms for this size wire. In this connection it should be noted that not all of the tension is due to the die as the wire was bent 5 times in the calorimeter about the pulleys and from the bobbin; further, it was found advisable for smooth operation to have a slight friction on bobbin *I* to insure straightening of the wire before entering the die. Most of this work energy appears as cold work in the wire but a small indeterminate amount was simple friction. All is accounted for, however, since it occurs within the calorimeter can.

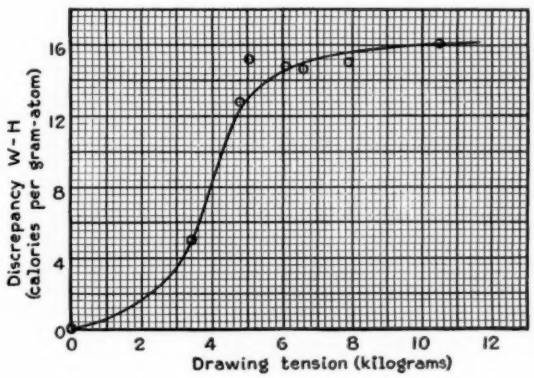

FIG. 2. Effect of tension on apparent energy storage in drawing No. 18 copper wire.

It must be true that at zero tension the discrepancy between work and heat would also be zero, whence a crude plot of discrepancy between work and heat *vs.* tension may be drawn, as in Fig. 2.

The experiments on copper probably are accurate on the average, to within 0.4 percent.

Part IV. Changes of Density due to Comminution

It is strange that no serious attempt seems to have been made in the past to correlate density changes due to comminution with the supposed storage of energy in crystals. Compressibility β of a material is defined as $\beta=(1/v_0)dv/dp$, where v_0 is the original volume and dp the pressure increment. If it is assumed that the work energy stored in a system of crystalline particles due to comminution is the equivalent of that required to compress it to the same state, then

$$\beta v_0\int_{p_0}^{p} pdp=-\int pdv=\int_0^w dw \text{ (work done on the system)}$$

whence

$$p^2-p_0^2=2w/v_0\beta$$

but $p^2-p_0^2$ will differ but little from $(\Delta p)^2$ in the case of liquids and solids when p_0 is near 1 atmosphere and for appreciable volume changes. Then quite closely

$$-\Delta v/v_0=(2w\beta/v_0)^{\frac{1}{2}} \quad \text{or} \quad w=(v_0/2\beta)(\Delta v/v_0)^2.$$

These equations should enable the density change to be calculated when the work "storage" is known, or conversely, fix the limits of possible "storage" whose measured density changes are determinable experimentally. We may, for example, calculate the expected density change based on the "surface-energy" measurements for sodium chloride of Lipsett, Johnson and Maass,[10] who gave 395 ergs per sq. cm for particles of 1-micron average size, corresponding to 15.3 calories per mole. Thus for sodium chloride, with a compressibility of $43.2\cdot10^{-7}$ (pressure in atmospheres) and a density of 2.15, we find $\Delta v/v_0=-0.014$, indicating that if the "surface-energy" figure is correct the density of the 1-micron crystals should be 1.4 percent greater than for large crystals, a change which certainly is easily detectable.

Considerations of this sort caused us to make precise density determinations of the various samples with which we worked. Carbon tetrachloride was used as the medium for these determinations, and the sample selected was shown to have a density of 1.58244 at 26.00°C, which compares well with the figure 1.58248 obtained by interpolation from the data of Timmermans and Martin.[11] The specific-gravity bottle containing the density sample was filled in a vacuum desiccator, the tetrachloride being boiled at 25–20°C to insure elimination of occluded gas. Table XI shows the results of these determinations.

Table XI. *Densities of samples used, grams/cm³, vacuum basis.*

No.	Material	Form	Density A.D. of M.	Temp. of determination
1	Calcite	0.8 mm particles	2.7133±0.0001	25.0°
2	Calcite	0.065 mm particles	2.7131±0.0001	25.0
3	Calcite	0.5 micron particles	2.6956±0.0003	25.0
4	Hydrated lime	Paste	(2.078)	
3c	Calcite	0.5 micron, corrected	2.7236	
5	Copper	No. 32 wire, annealed	8.9209±0.0005	21.2
6	Copper	No. 32 wire, hard-drawn	8.9140±0.0002	22.0
7	Aluminum	No. 32 wire, annealed	2.7147±0.0001	21.2
8	Copper	No. 32 wire, hard-drawn	2.7111±0.0002	21.9

The question of the correction of the density of 0.5-micron calcite, shown in line 3 of Table XI, for the $Ca(OH)_2$ and H_2O found by the analysis, was difficult. We finally hydrated some quicklime with an amount of water corresponding to the analysis of the impurity and made the rough density determination of line 4. The substance so prepared was a plastic mass that could not have uniform density and certainly was not in the same form as the film of impurity on the surface of the calcite particles, which had been dried at 105°C. However, by applying the result for the hydrated lime on the basis of additive *volumes* of impurity the maximum possible density of the fine calcite may be estimated in corrected form as given in line 3*c*.

These figures give for the possible change $\Delta v/v_0=0.0038$ in the formula derived from compressibility and if the compressibility is taken as $1.35\cdot10^{-6}$ we find the maximum possible energy storage to be 4.8 calories per $CaCO_3$, a figure just slightly less than the experimental error of the heat-of-solution experiments. It is highly probable, however, that the density has been overcorrected by the above estimate, since the true density of the surface film of impurity must be greater than the figure obtained by

[10] Lipsett, Johnson and Maass, J. Am. Chem. Soc. **49**, 1948 (1927).

[11] Timmermans and Martin, J. chim. Phys. **23**, 733 (1926).

measurement of the hydrated lime-water mixture; if the true figure were obtainable, a lower corrected density than 2.7236 for 0.5-micron material would result and the possible energy storage would then be less than 4.8 calories.[12]

In the case of the metallic wires, the hard-drawn material is less dense than the annealed and presumably recrystallized metal. This makes $\Delta v/v_0$ of the wrong sign for compression of the crystal lattice. However, it is obvious from the second form of the derived equation that energy can be stored by compression or expansion and we have therefore calculated the maximum storage of energy due to lattice distortion in a similar manner. Using $7.42 \cdot 10^{-7}$ and $13.85 \cdot 10^{-7}$ for the compressibilities of copper and aluminum when the pressure is in atmospheres, we find by application of the second form of the equation that the maximum storage of energy which can be accounted for on the basis of observed densities is 0.06 cal./g-atom for copper, and 0.15 cal./g-atom for aluminum, figures which are much less than the observed discrepancies 14.8 and 4.1 cal. in the wire-drawing experiments, and are indeed beyond the limit of conceivable accuracy of measurement by the methods obviously available. If the density of wires of this size is uniform throughout the cross section, the conclusion that the discrepancies found cannot represent energy stored by lattice distortion of pure crystalline metals seems valid. In cold-worked sections of larger size there seems to be unmistakable evidence in the literature for some variation in density, but definite proof concerning the quantitative relationships involved must await further experimental work. It seems improbable that a sufficient variation in density can be present in wires of this size adequate to explain the observed energy discrepancies.

[12] The overcorrection of density and heat of solution results for fine material is explainable by the failure to use correct figures for the density and heat of solution of the adsorbed film. When lime was hydrated with the amount of water corresponding to the analysis of 0.5-micron calcite a plastic mass containing free water was formed but material of similar properties certainly did not exist at the surface of the fine calcite crystals, which had been dried at 105°C. The pseudohydrate corresponding to the analysis must exist only as an adsorbed film, as Thorvaldson and Brown showed that no hydrate of lime other than $1H_2O : 1CaO$ forms normally at 21°C. Both strontium and barium oxides, however, form octahydrated crystals with the evolution of heat when water is added to the lower hydrate forms. Hence the heat of solution of the pseudohydrate is less and its density greater than for the normal hydrate form; if correct figures could be obtained they would tend to cause greater concordance between the corrected figures for fine calcite compared to coarse.

Part V. Meaning of Results

If the direct results of our experimental work are summarized, the conclusions would be as follows:

1. No evidence for increase of intrinsic energy of calcite due to comminution to 0.5-micron size could be found by heat-of-solution experiments; if such increase exists, it is less than 0.2 percent of the heat of solution and probably outside the limits of direct experimental disclosure.

2. Previous measurements purporting to show a considerable and readily detectable increase of intrinsic energy by this method are in error because of failure to correct for the change of composition produced in the sample by comminution.

3. We suspect, but have not proved, that previous measurements on other materials, by heat-of-solution methods, may be in error for the same reason and we would not accept such measurements unless adequate analytic evidence were adduced to prove that uncontaminated samples of very fine particles had been or can be produced.

4. It has been shown, to us, conclusively, that single crystals and hard-drawn and annealed specimens of copper and aluminum do not show differences of measurable entropy at 298°K greater than a few tenths percent, representing the accuracy of measurement, and that any actual difference must be accounted for by zero-point entropy.

5. Comparison of work and heat in the deformation of metallic crystals of copper and aluminum shows that only when carefully annealed samples are used can a discrepancy between work and heat be shown to exist. This discrepancy, for a given degree of cold working, is directly proportional to the mass of metal. It is not directly proportional to the degree of cold working but reaches a nearly constant value when a certain rather indefinite degree of cold work has been accomplished.

An important conclusion of our experimental work is that any rigorous demonstration of measured differences in the properties of pure crystalline materials in different states of subdivision must prove that no change of homogeneity has accompanied the comminution. In the case of the calcite we have direct proof that the supposed increase of intrinsic energy was due to a change in composition rather than distortion of the crystal lattice. In the case of the deformation of the metallic crystals of copper and aluminum the evidence is less direct and not obtainable by chemical analysis but the hypothesis that the process of cold working produces a change of state of *part* of the metal is the only one fitting the experimental facts, including the density relations.

A qualitative experiment which we performed seems illuminating. In connection with the use of the slip-thermel for measuring the loss of sensible heat in the wire withdrawn from the calorimeter, measurements were made to show that the tension in the wire constituting part of the thermel did not produce appreciable errors. Samples of the two wires (copper and aluminum) were placed upon a frame in such a manner as to constitute a thermel, strained copper *vs.* annealed copper, and strained aluminum *vs.* annealed aluminum. The frame work was partly immersed in liquid air and tension applied nearly to the rupture point of the wire, the thermal e.m.f. being noted. A typical test on aluminum was as follows: 0 tension, 3.50 microvolts e.m.f., all due to parasitic e.m.f.'s. When the tension was increased gradually to 5.5 kg the e.m.f. was 1.90μv, that is, the e.m.f. due to tension was 1.60μv. When the strain was removed the e.m.f. returned to 3.22μv; brought back to 5.5 kg the thermel read 1.88μv and back to zero tension, 3.22μv. In the case of copper, 0 tension, -0.60μv, 8.0 kg tension $+0.70\mu$v, back to zero tension -0.70μv.

The thermal e.m.f. due to strain was negligible as far as the slip-thermel readings were concerned, since practically constant tension was maintained during the use of the couple. Present interest centers in the fact that when the strain was removed the residual effect was only 0.28μv for aluminum and 0.10μv for copper in the first test and after the first straining later trials showed no further effect if the original stress was not passed in succeeding tests.

From this experiment it seemed probable that if strictly pure metal were used no parasitic e.m.f.'s could be produced. We proceeded to draw a wire from spectroscopically pure zinc containing less than 0.0001 percent impurity, as the purest metal available. The wire was annealed carefully before test. The e.m.f. with zero strain was $+1.15\mu$v, with 1.0 kg tension $+0.50\mu$v, back to zero strain $+0.75\mu$v. The use of *chemically* pure metal did not eliminate the parasitic e.m.f.'s nor residual effects and since these could be due only to inhomogeneities we conclude that the inhomogeneity is *physical*. There are no allotropic forms of pure crystalline zinc, whence the inhomogeneity was either crystal orientation or due to the appearance of a form of zinc which was not crystalline and which we shall call the ω form, without specifying its nature at present. Since the original wire was carefully annealed, we ascribe the $+1.15\mu$v parasitic e.m.f. to the effect of crystal orientation, the ω form presumably being absent because of recrystallization but we ascribe $1.15-0.75=0.40\mu$v residual difference to the appearance of a new inhomogeneity produced by strain.

Unannealed wire of spectroscopically pure zinc is extremely brittle at liquid-air temperatures but when 0.05 percent lead was added to spectroscopically pure zinc and a new wire produced, the lead-containing wire had high ductility at liquid-air temperatures. Since it was still largely crystalline zinc, we conclude that the brittleness at this temperature is not due entirely to the properties of normal crystalline zinc but to the ω form produced. Thoroughly annealed wire (recrystallized) was brittle, because of grain growth; cast rods of spectroscopically pure zinc cannot be directly drawn, but a small amount of swaging produces ductility, so that a $\frac{1}{4}$ inch rod can be drawn after swaging to No. 32 wire without annealing and with an apparent increase of ductility. The hypothesis supposes the ductility to be due to the ω form in the spectroscopically pure metal and to lead in the intercrystalline slip planes when the impure wire was made.

It is natural to associate the properties of the ω form produced by stresses beyond the elastic

limit on pure metallic crystals with those of an amorphous metal or supercooled liquid, a theory advanced by Beilby[13] but severely criticized by physical metallurgists.[14] Our tests on the discrepancy between work and heat in drawing enable us to make approximate estimates of the amount of ω-phase metal by two independent methods.

Consider first the densities of hard-drawn and annealed copper and aluminum. From the measurements of Bornemann and Sauerwald[15] the density of liquid copper at the melting point is 7.982 and that of solid copper at the same temperature 8.350. According to Hidnert[16] the thermal expansiveness of hard-drawn copper changes less rapidly with the temperature than the same copper annealed. Therefore the difference of density of pure crystalline copper *vs.* the ω form at room temperature is concluded to be greater than $8.350-7.982=0.368$ and less than $8.920-7.982=0.938$. Then the percentage of ω form in the hard-drawn wire used by us is less than $(8.9209-8.9140)/0.368=1.9$ percent, and greater than $(8.9209-8.9140)/0.938=0.74$ percent.

Similarly, in the case of aluminum, Bornemann and Sauerwald give data leading to the density 2.397 for liquid metal at the melting point and 2.558 for the solid, whence the observed density differences lead to the conclusion that the ω phase present is less than 2.2 percent and more than 1.1 percent.

As an alternative method of calculating the amount of the ω phase, comparison may be made between the heat of fusion for the metal in question and the differences of heat and work observed in the drawing experiments. The heats of fusion at the melting point of copper and aluminum are 3110 and 2550 calories; corrected to ordinary temperatures in a conventional manner and assuming that the specific heat of the supercooled liquid is constant, the heats at 25°C would be approximately 2300 for copper and 2400 for aluminum, whence the calculated content of the ω phase is $14.8/2300=0.64$ percent for copper and $4.1/2400=0.17$ percent for aluminum.

Comparison of these results shows that while the calculated content of the ω phase is of the same general order of magnitude by the two methods, the figures can scarcely be said to confirm satisfactorily the hypothesis that the ω phase is essentially supercooled liquid. It should be noted, however, that the density results were obtained on finer wire (No. 32) than the energy discrepancy (No. 18 wire) and it may be supposed that the amount of the ω phase bears some nearly inverse functional relationship to the size of crystal particles formed by the drawing process.

In conclusion, we can only describe our work as having failed to disclose, by careful measurements of the energy changes in comminution, any change in energy content of certain crystal lattices due to decrease of particle or crystal size which is not ascribable to lack of homogeneity of small crystals. Such calculations of surface energy as those of Born and Stern[17] or their later modifications by Lennard-Jones and Dent[18] or by Dent[19] on the surface energies of alkali halide crystals, seem to make the implicit assumptions that crystals may exist without other inhomogeneity than some rather minor distortion of the crystal boundary, or its surface ions, but practically it remains to be proved that such a situation is either common or possible in nature. If chemical inhomogeneity (adsorbed films) or physical inhomogeneity (polymorphic change) is, as may be supposed, the inevitable concomitant of decrease of particle size, such calculations seem of little value in describing the properties of actual materials.

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[13] Beilby, *Aggregation and Flow of Solids*, Macmillan Company, London (1921).

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The Surface Tension of Debye-Hückel Electrolytes

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As has been shown by Wagner, the increase of the surface tension caused by the addition of a strong electrolyte to water is mainly due to the repulsion of ions from the surface by the electrostatic image force. Due to the shielding action of the "ionic atmospheres," of radius $1/\kappa$, the image force is appreciable only within distances of the order $1/\kappa$ from the surface. The computations become very complicated if, as Wagner did, one attempts to allow for the variation of κ with the depth in accordance with the decreased concentration of ions in the surface layers. Fortunately, a detailed analysis of the problem shows that this refinement may be dispensed with as a first approximation, and that the formulas thus derived will be accurate for not too high concentrations. The same analysis tends to show that Wagner's procedure supplies only a part of the intended correction, so that the results will be applicable only over a slightly wider range of concentrations than the convenient explicit formulas which are derived from the simplified theory. In the limit of low concentrations, the increment of the surface tension is proportional to $c \log c$. The theory accounts reasonably well for the observed surface tensions up to 0.2 N concentration. The discrepancies, while partly due to mathematical approximations, may be of some physical significance and would mean that for small distances the repulsion from the surface is greater than expected from Coulomb's law. Nevertheless, the agreement obtained verifies Coulomb's law for univalent ions at distances greater than a molecular diameter from the surface.

INTRODUCTION

IT was first shown by Heydweiller and his coworkers[1] that the solutions of inorganic salts in water have greater surface tensions than that of the pure solvent. Thermodynamically interpreted, this result indicates a deficiency of solute in the interface region. Since different uni-univalent salts, added in equivalent amounts, cause about the same increment of the surface tension, the effect is apparently determined by the charges of the ions. Heydweiller sought an explanation in the electrostatic attraction between the ions. However, after Debye and Hückel had provided a workable basis for the computation of interionic forces, Wagner[2] was able to show that the principal effect is due to the "image force" near the boundary between two dielectrics, e.g., water and air. In this picture, the "ionic atmospheres" of Debye and Hückel are called upon to limit the depth of the layer in which the ions are repelled from the surface.

The mathematical problems involved are very difficult. Wagner was able to formulate differential equations comparable in accuracy to the approximation of Debye and Hückel. After a further simplifying approximation, Wagner obtained by integration an implicit formula for the adsorption potential. From this stage, he had to proceed by laborious numerical integrations in order to compute the deficiency of solute in the interface region, and finally the surface tension.

In the present work, we shall not attempt to improve the accuracy of Wagner's computations. Instead, we shall adopt a further simplification which we believe not to impair greatly the accuracy, and which leads to explicit formulas that can be easily handled. Our main result is the following limiting law for the surface tension:

$$\sigma = \sigma_0 + \text{const.} \times c \log (\text{const.}/c). \qquad (1)$$

Like Wagner, we shall limit ourselves to binary electrolytes, although our computations can be extended without much difficulty to asymmetric valence types as well.

THE STRUCTURE OF THE INTERFACE LAYER

According to general kinetic principles, the concentration $c(x)$ of solute at a distance x from the boundary depends on the work $W(x)$ required to bring a molecule of the solute—or an ion, as the case may be—from the interior of the solution to a point at the depth x. The connection between $c(x)$ and the *adsorption potential* $W(x)$

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[1] Heydweiller, Ann. d. Physik (4) **33**, 145 (1910).

[2] Wagner, Phys. Zeits. **25**, 474 (1924).

is given by the Maxwell-Boltzmann formula

$$c(x)=c\exp(-W(x)/kT), \tag{2}$$

where $c=c(\infty)$ denotes the concentration in the interior. In the case of an electrolyte, every species i of ions should be considered as a separate kind of molecule, which may possess its individual adsorption potential $W_i(x)$. Only for binary electrolytes, the adsorption potentials $W_1(x)$ and $W_2(x)$ of anions and cations are apt to be very nearly equal.

We now proceed to compute $W(x)$ from Wagner's picture. First, let us consider a single ion of charge e, in a medium of dielectric constant D, at a distance x from a plane boundary against another medium of dielectric constant $D'=1$ (air). The electrostatic potential ψ in the medium containing the ion will be

$$\psi=\frac{e}{Dr_1}+\frac{(D-1)}{(D+1)}\frac{e}{Dr_2}, \tag{3}$$

where r_1 denotes the distance from the ion, and r_2 the distance from its image with regard to the boundary (see Fig. 1). The second term in (3) is due to the fictitious charge at the boundary, which exerts the force

$$-\frac{\partial W}{\partial x}=\left[\frac{(D-1)}{(D+1)}\frac{e^2}{Dr_2^2}\right]_{r_2=2x}=\frac{(D-1)}{(D+1)}\frac{e^2}{4Dx^2}$$

on the ion. The potential of this force equals

$$W(x)=\frac{(D-D')}{(D+D')}\frac{e^2}{4Dx}=\frac{(D-1)}{(D+1)}\frac{e^2}{4Dx}. \tag{4}$$

As pointed out by Wagner, an adsorption potential of the type (4) would cause an infinite increment of the surface tension, because the adsorbed amount would be

$$\Lambda=c\int^{\infty}(-1+e^{-W/kT})dx=-\infty.$$

The paradox readily resolves itself when we take into account the screening of the electrostatic force by the other ions. According to the theory developed by Gouy and by Debye and Hückel,[3] the screening by an electrolytic conductor limits

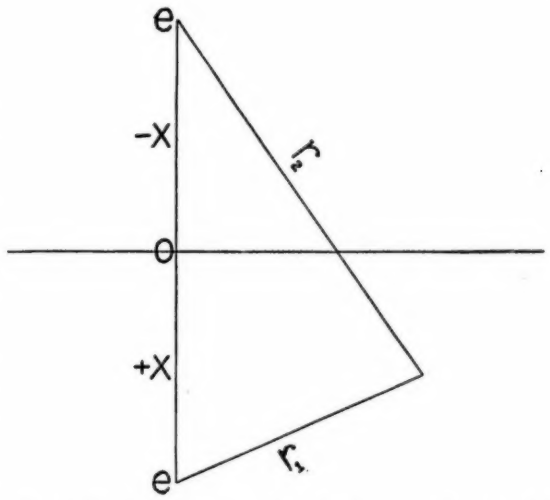

FIG. 1. Diagram for computing the electrostatic potential due to a point charge e and its image $[(D-1)/(D+1)]e \sim e$.

the effective range of electrostatic forces to a distance $1/\kappa$, where

$$\kappa^2=(4\pi/DkT)\sum_i n_i e_i^2. \tag{5}$$

Here, $n_1, n_2, \cdots$ denote the numbers of ions with the charges $e_1, e_2, \cdots$ per unit volume. Instead of the Laplace equation

$$\Delta\psi=0,$$

the electrostatic potential obeys the differential equation[4]

$$\Delta\psi-\kappa^2\psi=0. \tag{6}$$

We must now remember that the concentration of electrolyte near the surface is less than that in the interior of the solution. In Eq. (6), therefore, the value of κ^2 at a given point depends on the distance ξ from the surface to this point according to Eqs. (5) and (2). In cylindrical coordinates (ξ, λ) we should write

$$\Delta\psi=\frac{\partial^2\psi}{\partial\xi^2}+\frac{1}{\lambda}\frac{\partial}{\partial\lambda}\left(\lambda\frac{\partial\psi}{\partial\lambda}\right)=\kappa^2(\xi)\psi. \tag{7}$$

We face the task of solving this equation for the case that an ion of charge e is present at the point $(\xi=x, \lambda=0)$. For $\xi>0$, $\kappa^2(\xi)$ is given by Eqs. (5) and (2), while for $\xi<0$, $\kappa^2(\xi)=0$. At the boundary $\xi=0$, ψ is continuous and $\partial\psi/\partial\xi$ changes by the factor D.

[3] Gouy, J. de Physique (4) **9**, 457 (1910); Debye and Hückel, Phys. Zeits. **24**, 185 (1923).

[4] Regarding the approximate nature of this equation, see Onsager, Chem. Rev. **13**, 73 (1933).

In order to obtain an approximate solution of this problem, Wagner replaced the dielectric constant $D'=1$ of the adjoining air by

$$D'=0. \tag{8}$$

It can be shown that the relative error in W due to this approximation is less than $2/(D+1)$. If desired, the corrections to W due to the finite value of D' can be computed by expansion in integrals of cylinder functions.

Wagner made one more approximation, which served to remedy the most inconvenient feature of Eq. (7), that is the variation of κ^2 with ξ. For this purpose, he replaced $\kappa^2(\xi)$ throughout by $\kappa^2(x)$. The resulting approximate equation can be readily integrated, but leads to an implicit equation for $W(x)$. Substantially simpler results can be obtained by the more drastic approximation[5]

$$\kappa^2(\xi)\sim\kappa^2(\infty)=\kappa^2. \tag{9}$$

Let us try to estimate the errors involved by the two approximations. First, we note that Eq. (4), where the shielding is entirely neglected, must give us an overestimate of W, and therefore an underestimate of $\kappa^2(\xi)$. It makes no important difference if we adopt Wagner's first approximation $D'=0$, whereby Eq. (4) becomes

$$W(x)=e^2/4Dx.$$

We shall write

$$q=e^2/2DkT. \tag{10}$$

For univalent ions in water, the length q equals 3.5×10^{-8} cm. If the concentration of the electrolyte in the interior is c, then at a distance ξ from the surface it will be at least

$$c\exp(-q/2\xi)\leqq c(\xi). \tag{11}$$

Therefore, as soon as $\xi\geqq q$, $\kappa^2(\xi)$ is certainly comparable to $\kappa^2(\infty)$. It also follows that, if

$$\kappa q<1,$$

the shielding range near the surface will be of the same order of magnitude as that in the interior of the solution. In conjunction with Eq. (11), this observation provides a basis for estimating the total deficiency $(-\Lambda)$ of electrolyte per unit surface area. On account of the shielding, we need only consider a layer of the depth m/κ, where m is some constant comparable to unity. For $x<m/\kappa$, we apply the estimate (11), and obtain

$$-\Lambda\sim c\int_0^{m/\kappa}[1-\exp(-q/2x)]dx \sim\tfrac{1}{2}cq\log(m/\kappa q).$$

This deficiency is equivalent to a layer of the thickness

$$\delta\sim\tfrac{1}{2}q\log(m/\kappa q), \tag{12}$$

entirely depleted of solute. With very little actual computation, we have thus, in effect, demonstrated the general form of the limiting law (1) for low concentrations. It is important that although δ increases logarithmically when κq approaches zero, still δ increases much less rapidly than $1/\kappa$, so that

$$\kappa\delta\ll1 \quad\text{when}\quad \kappa q\ll1. \tag{13}$$

We now have to consider how the decreased concentration of electrolyte near the surface will affect the shielding of the electrostatic force between an ion and its image. An exact solution of the problem is very difficult; but it can be shown that the shielding depends mainly on the concentrations in the layers between the ion and the surface. In case of a constant "shielding coefficient" κ, the absorption of the force-lines introduces a factor

$$\exp(-\kappa r)$$

in the potential of a point source. An ion at the distance x from the surface is at the distance $2x$ from its image, so that the corresponding shielding factor would be

$$\exp(-2\kappa x). \tag{14}$$

Now if a layer of the thickness δ contributes nothing to the shielding, then the exponent in Eq. (14) will be changed (at the worst) to $2(x-\delta)\kappa$; so that the relative error involved by the approximation (9) is not greater than

$$e^{2\kappa\delta}-1\sim2\kappa\delta\sim\Delta\Lambda/\Lambda. \tag{15}$$

We have shown already (formulas (12) and (13)) that an error of this order of magnitude may be neglected for sufficiently low concentrations of electrolyte.

[5] Oka (Proc. Phys.-Math. Soc. Japan **14**, 649 (1932); ibid. **15**, 407 (1933)) adopted this equation as a starting point for his computation. Due to an oversight on his part, he obtained twice our value for the adsorption potential.

This analysis throws light on Wagner's approximation as well. In his computation he replaces $\kappa^2(\xi)$ throughout by $\kappa^2(x)$. It seems probable that this approximation still involves an overestimate of the "effective" κ, considering that the shielding is mainly effected by the region $0<\xi<x$, where $c(\xi)<c(x)$. We therefore believe that Wagner's error, although smaller than ours, is still of the same order of magnitude, given by (15), and in the same direction. Both computations lead to overestimates of κ, with consequent underestimates of W, Λ, and finally of the increment of the surface tension. Both computations are correct in the limit of low concentrations.

We now compute the adsorption potential with the aid of the approximations

$$D'=0, \quad \kappa^2(\xi)=\kappa^2(\infty)=\kappa^2.$$

With these assumptions, and for the case of point ions with charges e, e present at $(\xi=x, \lambda=0)$ and $(\xi=-x, \lambda=0)$, the solution of the differential Eq. (6),

$$\Delta\psi-\kappa^2\psi=0,$$

assumes the simple form

$$\psi=ee^{-\kappa r_1}/Dr_1+ee^{-\kappa r_2}/Dr_2. \tag{16}$$

Here, ψ is the electrostatic potential in the medium containing the ion, and the second term arises from the fictitious surface charge, which exerts the force

$$-\frac{\partial W}{\partial x}=-\frac{\partial}{\partial r_2}\left(\frac{e^2e^{-\kappa r_2}}{Dr_2}\right)_{r_2=2x}=-\frac{\partial}{\partial x}\left(\frac{e^2e^{-2\kappa x}}{4Dx}\right)$$

on the ion. Consequently, the adsorption potential $W(x)$ is

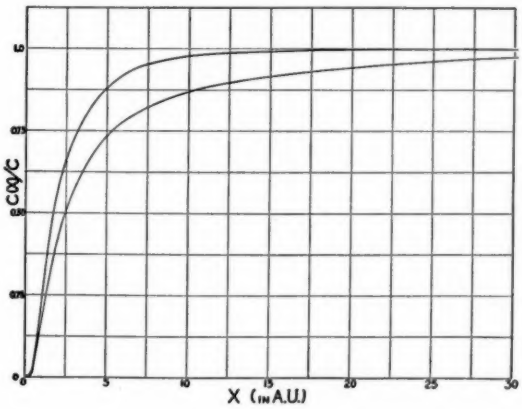

FIG. 2. Density distribution in the interface region for uni-univalent electrolytes. The concentrations are 0.1 mol./l. (upper curve) and 0.001 mol./l.

$$W(x)=\int_{\infty}^{x}\frac{\partial W}{\partial x}dx=\frac{e^2e^{-2\kappa x}}{4Dx}. \tag{17}$$

Combining expressions (2) and (17) we obtain

$$c(x)/c=e^{-e^2e^{-2\kappa x}/4DkTx}=e^{-qe^{-2\kappa x}/2x}. \tag{18}$$

This density distribution is shown in Fig. 2, for uni-univalent electrolytes and for concentrations of 0.1 (upper curve) and 0.001 mol./l.; the corresponding values of the shielding range $1/\kappa$ are 10A and 100A, respectively.

If we consider the size of the ions as well, and introduce the Debye-Hückel "mean distance of approach" a which we may take, with Wagner, as small compared to x, formula (17) is modified as follows:

$$W(x)=\frac{e^{\kappa a}}{1+\kappa a}\frac{e^2}{4Dx}e^{-2\kappa x}. \tag{19}$$

COMPUTATION OF THE SURFACE TENSION INCREASE

The total amount "negatively" adsorbed per unit change in surface area is thus given by

$$\Lambda=c\int_0^{\infty}(e^{-(e^{\kappa a}/1+\kappa a)(e^2/4DkTx)e^{-2\kappa x}}-1)dx. \tag{20}$$

If, for convenience, we substitute

$$q=e^2/2DkT; \qquad h=[e^{\kappa a}/(1+\kappa a)]\kappa q; \qquad u=2\kappa x, \tag{21}$$

expression (20) becomes

$$\Lambda=(c/2\kappa)\int_0^\infty (e^{-he^{-u}/u}-1)du=(c/2\kappa)I. \tag{22}$$

First, we proceed to evaluate I by integration in the complex plane.[6] Let $z=-u$; then,

$$I=\int_{-\infty}^{-0}(e^{he^z/z}-1)dz. \tag{23}$$

Consider the integral

$$\Phi=(1/2\pi i)\int_{-\infty}^{(0+)}(e^{he^z/z}-1)(e^z/z)^\beta dz, \tag{24}$$

where $-1<\beta<1$, and $|\arg(z)|\leqq\pi$; the path of integration runs from $-\infty$ counterclockwise around the origin and back to $-\infty$. In analogy with Hankel's treatment of the gamma function,[7] the contour integral (24) may be broken up as follows:

$$\Phi=(1/2\pi i)\int_{-\infty}^{-0}(e^{he^z/z}-1)e^{\beta z}\{(-z)^{-\beta}e^{\pi i\beta}-(-z)^{-\beta}e^{-\pi i\beta}\}dz$$
$$+(1/2\pi i)\int_{-0}^{(0+)}(e^{he^z/z}-1)e^{\beta z}z^{-\beta}dz=\Phi_1+\Phi_2. \tag{25}$$

Since

$$\Phi_1=(\sin\pi\beta/\pi)\int_{-\infty}^{-0}(e^{he^z/z}-1)e^{\beta z}(-z)^{-\beta}dz,$$

it can be easily seen that

$$\left[\frac{\partial\Phi_1(\beta)}{\partial\beta}\right]_{\beta=0}=\lim_{\beta\to0}\frac{1}{\beta}\Phi_1(\beta)=\int_{-\infty}^{-0}(e^{he^z/z}-1)dz=I,\quad\text{or}\quad I=\lim_{\beta\to0}\frac{1}{\beta}(\Phi-\Phi_2)=\left[\frac{\partial}{\partial\beta}(\Phi-\Phi_2)\right]_{\beta=0}. \tag{26}$$

Now, with the aid of Hankel's formula[7] for the gamma function,

$$\Phi=(1/2\pi i)\int_{-\infty}^{(0+)}(e^{he^z/z}-1)(e^z/z)^\beta dz$$
$$=\sum_{n=1}^\infty\frac{h^n(n+\beta)^{n+\beta-1}}{n!}\cdot\frac{1}{2\pi i}\int_{-\infty}^{(0+)}e^{z(n+\beta)}(z(n+\beta))^{-(n+\beta)}d(z(n+\beta))$$
$$=\sum_{n=1}^\infty\frac{h^n(n+\beta)^{n+\beta-1}}{n!\Gamma(n+\beta)}=\sum_{n=1}^\infty\frac{h^n(n+\beta)^{n+\beta}}{n!\Gamma(n+\beta+1)}. \tag{27}$$

To handle the integral

$$\Phi_2=(1/2\pi i)\int_{-0}^{(0+)}(e^{he^z/z}-1)e^{\beta z}z^{-\beta}dz$$

we may substitute $e^z/z=1/t$, and by Lagrange's theorem[8] expand z in the following power series in t:

$$z=\sum_{n=1}^\infty(n^{n-1}/n!)t^n.$$

[6] This integration can also be carried out by expanding in modified Bessel functions of the second kind—a more laborious method.

[7] Whittaker and Watson, *A Course of Modern Analysis*, p. 244, §12.22, Cambridge University Press, 1927.

[8] Whittaker and Watson, reference 7, p. 132, §7.32.

By common criteria, the expansion is valid within the circle of convergence, $|t| \leqq e^{-1}$. Hence,

$$\Phi_2 = \sum_{n=1}^{\infty} \frac{n^n}{n!} \frac{1}{2\pi i} \int_{-0}^{(0+)} (e^{h/t} - 1) t^{n-\beta-1} dt$$

or, taking $1/t = v$,

$$\Phi_2 = \sum_{n=1}^{\infty} \frac{n^n}{n!} \frac{1}{2\pi i} \int_{-\infty}^{(0-)} (e^{hv} - 1) v^{\beta-n-1} (-dv) = \sum_{n=1}^{\infty} \frac{n^n h^{n-\beta}}{n!} \frac{1}{2\pi i} \int_{-\infty}^{(0+)} (e^{hv} - 1)(hv)^{\beta-n-1} d(hv)$$

$$= \sum_{n=1}^{\infty} \frac{n^n h^{n-\beta}}{n!} \frac{1}{2\pi i} \int_{-\infty}^{(0+)} e^{hv} (hv)^{\beta-n-1} d(hv) = \sum_{n=1}^{\infty} \frac{n^n h^{n-\beta}}{n!\Gamma(n-\beta+1)}. \quad (28)$$

From Eqs. (27) and (28)

$$\left(\frac{\partial \Phi}{\partial \beta}\right)_{\beta=0} = \sum_{n=1}^{\infty} \frac{h^n}{n!} \frac{\partial}{\partial n}\left(\frac{n^n}{\Gamma(n+1)}\right); \qquad \left(\frac{\partial \Phi_2}{\partial \beta}\right)_{\beta=0} = -\sum_{n=1}^{\infty} \frac{n^n}{n!} \frac{\partial}{\partial n}\left(\frac{h^n}{\Gamma(n+1)}\right).$$

Therefore, expression (26) gives

$$\int_0^{\infty} (e^{-he^{-u/u}} - 1) du = I = \lim_{\beta \to 0} \frac{1}{\beta}(\Phi - \Phi_2) = \sum_{n=1}^{\infty} \left\{ \frac{h^n}{\Gamma(n+1)} \frac{\partial}{\partial n}\left(\frac{n^n}{\Gamma(n+1)}\right) + \frac{n^n}{\Gamma(n+1)} \frac{\partial}{\partial n}\left(\frac{h^n}{\Gamma(n+1)}\right) \right\}$$

$$= \sum_{n=1}^{\infty} \frac{\partial}{\partial n}\left\{ \frac{n^n h^n}{\Gamma(n+1)\Gamma(n+1)} \right\} = \sum_{n=1}^{\infty} \frac{n^n h^n}{n!n!} \left\{ \log_e (nh) + 1 - 2\frac{\Gamma'(n+1)}{\Gamma(n+1)} \right\}$$

$$= \sum_{n=1}^{\infty} \frac{n^n h^n}{n!n!} \left\{ \log_e (nh) + 1 + 2\gamma - 2\sum_{n=1}^{n} \frac{1}{n} \right\}, \quad (29)$$

where

$$\gamma = \text{Euler's constant} = 0.5772157 \cdots. \quad (30)$$

We shall write

$$g_n = \log_e n + 1 + 2\gamma - 2\sum_{n=1}^{n} \frac{1}{n}. \quad (31)$$

By combining formulas (22), (29) and (31), we finally have for Λ,

$$\Lambda = \frac{c}{2\kappa} \sum_{n=1}^{\infty} \frac{n^n h^n}{n!n!} (\log_e h + g_n). \quad (32)$$

It is clear that, for binary electrolytes, Λ denotes the number of moles of solute "negatively" adsorbed per unit increase of interface area. The relation between the change of surface tension and Λ is given by the adsorption equation of Gibbs, which can be put into the form[9]

$$\Lambda = -(\partial \sigma / \partial \bar{F}_2)_s = -\partial \sigma / RT \partial \log_e a_2; \quad (33)$$

s is the area of the surface, $\bar{F}_2$ and a_2, the partial molal free energy and the activity of the solute, respectively. Hence, from Eqs. (32) and (33),

$$d\sigma = -RTd \log_e a_2 \frac{c}{2\kappa} \sum_{n=1}^{\infty} \frac{n^n h^n}{n!n!} (\log_e h + g_n), \quad (34)$$

where, for the electrolytes considered, a_2 is defined by

[9] Lewis and Randall, *Thermodynamics*, p. 250, McGraw-Hill, 1923.

$$\log_e a_2 = 2(\log_e c + \log_e f). \tag{35}$$

The Debye-Hückel expression for f, the mean activity coefficient of the solute, is

$$\log_e f = -e^2\kappa/2DkT(1+\kappa a) = -q\kappa/(1+\kappa a), \tag{36}$$

whence $d\log_e f = -[q/(1+\kappa a)^2]d\kappa$; and, since $\kappa^2 = (8\pi Ne^2/DkT)c = 16\pi Nqc$, Eq. (34) readily assumes the form

$$d\sigma = -\frac{kT}{16\pi q}\sum_{n=1}^{\infty}\frac{n^n}{n!n!}\left(2-\frac{q\kappa}{(1+\kappa a)^2}\right)h^n(\log_e h + g_n)d\kappa. \tag{37}$$

If we adopt the approximation $a=0$, which amounts to the well-known Debye-Hückel procedure of treating the ions as point charges, the individual terms in the series can be integrated in closed form. We shall write

$$y = \kappa q = h; \tag{38}$$

then the surface tension σ of a solution containing c moles of electrolyte per cc is given by

$$\sigma - \sigma_0 = \Delta\sigma = -\frac{kT}{16\pi q^2}\sum_{n=1}^{\infty}\frac{n^n}{n!n!}\int_0^y (2-y)y^n(\log_e y + g_n)dy$$

$$= -\frac{kT}{16\pi q^2}\sum_{n=1}^{\infty}\frac{n^n}{n!n!}\left\{\frac{2y^{n+1}}{n+1}\left(\log_e y - \frac{1}{n+1} + g_n\right) - \frac{y^{n+2}}{n+2}\left(\log_e y - \frac{1}{n+2} + g_n\right)\right\}$$

$$\equiv \frac{kT}{16\pi q^2}(Y_c + Y_f) \equiv \frac{kT}{16\pi q^2}Y. \tag{39}$$

In the limit, neglecting the contribution from the activity coefficient,

$$\Delta\sigma = -(kT/16\pi q^2)y^2(\log_e y - \tfrac{1}{2} + g_1) = -(Ne^2/2D)c\{\log_e(\kappa q) - 0.34557\}, \tag{40}$$

where N denotes Avogadro's number. For uni-univalent electrolytes the limiting law becomes

$$\sigma = \sigma_0 + (79.517/D)m\log_{10}(1.143\times 10^{-13}(DT)^3/m); \tag{41}$$

m is the concentration of the solute in moles per liter. Thus, with water as the solvent, formula (41) gives

$$\Delta\sigma_{273} = 0.904m\log_{10}(1.585/m), \qquad \Delta\sigma_{293} = 0.989m\log_{10}(1.493/m), \tag{41a}$$

the subscripts in $\Delta\sigma$ indicating the absolute temperature.[10]

We shall confine our numerical computations to uni-univalent electrolytes in water. Inasmuch as the surface tension increment is extremely small for very low salt concentrations, the limiting law (41) cannot be tested directly. We may, however, employ formula (39), which can be easily modified to allow for the size of the ions. Numerical calculations show that the values for $\Delta\sigma$ are practically independent of the exact value chosen for a, the Debye-Hückel mean distance of approach for the ions, and hence, if we take for convenience

$$a = q = \epsilon^2/(2DkT) \tag{42}$$

($q_{273} = 3.457$A; $q_{293} = 3.527$A), we have

$$h = \kappa q(e^{\kappa q}/(1+\kappa q)) = y(e^y/(1+y)).$$

We then obtain from Eq. (37)

$$\Delta\sigma = (kT/16\pi q^2)(Y_c' + Y_f') = (kT/16\pi q^2)Y', \tag{43}$$

[10] The dielectric constants of water have been calculated from Wyman's equation (Phys. Rev. **35**, 623 (1930)), $D = 78.54[1-0.00460(t-25)+0.0000088(t-25)^2]$, where t is the temperature in degrees centigrade.

where

$$Y_c' = -\sum_{n=1}^{\infty} \frac{2n^n}{n!n!} \int_0^y y^n \left(\frac{e^y}{1+y}\right)^n \left\{\log_e \frac{y}{1+y} + y + g_n\right\} dy,$$

$$Y_f' = \sum_{n=1}^{\infty} \frac{n^n}{n!n!} \int_0^y \frac{y^{n+1}}{(1+y)^2} \left(\frac{e^y}{1+y}\right)^n \left\{\log_e \frac{y}{1+y} + y + g_n\right\} dy. \tag{43a}$$

The integrations can be performed by multiplying the absolutely convergent series e^{ny} and $(1+y)^{-m}$, $y^2<1$. Then all the integrals are reduced to an easily integrable single type, and the series involved converge very rapidly for the concentrations in which we are interested.

Expression (39) (or (43)) can be put into the useful form

$$\frac{Y}{y^2} = \frac{Y_c + Y_f}{y^2} = \frac{2\times 10^3 \sigma_0 D}{N\epsilon^2} \left(\frac{\Delta\sigma}{m\sigma_0}\right) \equiv A\Delta\alpha. \tag{44}$$

$\Delta\alpha$ is the increase in surface tension per mole divided by the surface tension of the solvent, and

$$y^2 = \kappa^2 q^2 = (1.746\times 10^{13}/(DT)^3)m \equiv Bm. \tag{44a}$$

The magnitudes of $A\Delta\alpha$ for concentrations up to about 0.18 mol./l., computed without and with allowance for the ionic diameter a, are given in parts I and II of Table I. The contributions to $A\Delta\alpha$

TABLE I. *Theoretical values of $A\Delta\alpha$ for uni-univalent electrolytes in water.*

I				II			
y^2	Y_c/y^2	Y_f/y^2	$A\Delta\alpha$	y^2	Y_c'/y^2	Y_f'/y^2	$A\Delta\alpha$
0.			∞	0.			∞
0.0063	3.048	−0.076	2.972				
0.0126	2.747	−0.097	2.650				
0.0189	2.576	−0.111	2.465				
0.0315	2.367	−0.134	2.233				
0.0378	2.295	−0.141	2.154	0.0378	2.308	−0.107	2.201
0.0630	2.095	−0.163	1.932	0.0850	2.003	−0.125	1.878
0.0944	1.944	−0.184	1.760				
0.1259	1.840	−0.203	1.637	0.1259	1.867	−0.132	1.735
0.1574	1.760	−0.217	1.543				
0.1889	1.697	−0.228	1.469	0.1963	1.718	−0.139	1.579
0.2014	1.675	−0.232	1.443				
0.2266	1.634	−0.241	1.394				

from the concentration factor and from the activity coefficient factor in the activity of the solute are shown separately.

The contribution to the surface tension increment from the linear term βc of the activity-coefficient expression

$$\log_e f = -q\kappa/(1+\kappa a) + \beta c,$$

where β is a constant characteristic of the individual electrolyte, is given by

$$\Delta\sigma_\beta = -\frac{2RT\beta}{(16\pi N)^2 q^2} \sum_{n=1}^{\infty} \frac{n^n q^n}{n!n!a^{n+3}} \int_0^{\kappa a} (\kappa a)^{n+2} \left(\frac{e^{\kappa a}}{1+\kappa a}\right)^n \left\{\log_e \frac{\kappa a}{1+\kappa a} + \kappa a + \log_e \frac{q}{a} + g_n\right\} d(\kappa a).$$

For the highest concentrations considered this total effect is found to be small, and hence individual differences between electrolytes have been neglected in the numerical computations. It has already been mentioned that differences in the value for a, the ionic diameter, hardly affect the numerical result. For example, at $m=0.1$, assuming $a=q=3.46$A, $A\Delta\alpha$ has the value 1.735; if we take $a=2.81$A, $A\Delta\alpha$, computed from formulas (37) and (44), is 1.715. At low concentrations, individual differences due to these two characteristics are still smaller.

Comparison with Experiment

That, for low concentrations, neither of the factors characterizing individual electrolytes (a and β) enters prominently in the theoretical expressions is in accord with the conclusion drawn by Heydweiller,[1] and more recently by Schwenker,[11] that for a given concentration the increase in surface tension is the same for all uni-univalent electrolytes examined, within the limits of the experimental error.

In Fig. 3, we have plotted the values of $A\Delta\alpha$

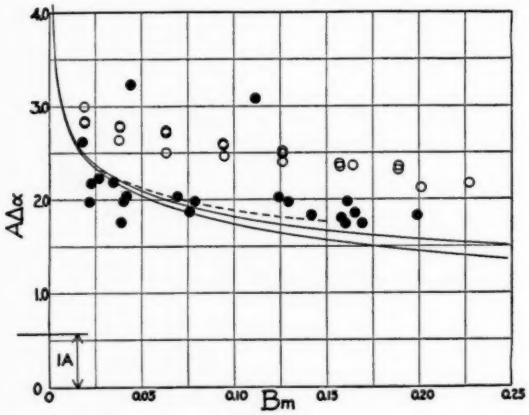

FIG. 3. Theoretical variation of $A\Delta\alpha$ for uni-univalent electrolytes (solid and dotted curves), and $A\Delta\alpha$ values from the available experimental data.

given in Table I against $y^2=Bm$; the upper curve shows the effect of introducing the size of the ions. The dotted curve has been drawn through the four points calculated by Wagner for $T=291$. The full dots correspond to the values experimentally determined by Heydweiller and his co-workers for LiCl, NaCl, KCl, NH_4Cl, $NaNO_3$ and KNO_3. The data of Schwenker (for LiCl, KCl and NaCl) are represented by the circles; his measurements were carried out at $T=273$. The values of the constants A and B (see Eqs. (44) and (44a)) for the two temperatures are (at $T=273$, $D=88.00$, $\sigma_0=75.597$ dynes/cm; at $T=291$, $D=81.103$, $\sigma_0=72.8$ dynes/cm)

$$\begin{aligned} A_{273}&=96.32; \quad B_{273}=1.259 \\ A_{291}&=85.49; \quad B_{291}=1.328. \end{aligned} \tag{45}$$

As a crude scale for comparing the magnitude of the total effect we have given the value for $A\Delta\alpha$ obtained on the assumption that $c(x)=c$ for $x>1$A, and $c(x)=0$ for $x<1$A (this value is 0.579 at $T=273$ and 0.568 at $T=291$).

The agreement between the data of Heydweiller and those of Schwenker leaves a great deal to be desired; probably, Schwenker's measurements represent an advanced technique. We must bear in mind, however, that the effect to be measured is quite small. Schwenker estimates that the relative error of his measurements is 0.011 percent, which, on the large scale of Fig. 3, corresponds to changes in $A\Delta\alpha$ of $0.0133/(Bm)$ units.

Examination of the data for the individual salts indicates that, for low concentrations, $\Delta\alpha$ increases rapidly with decreasing concentration, an observation which did not escape Heydweiller. Yet, the comparison between Schwenker's data and the theoretical curve is not entirely conclusive, partly due to the approximations made in the theory, and partly because of the experimental uncertainty. It is evident from the analysis given in a preceding section that an exact computation would raise the theoretical curve; also, it is possible that a revision of Schwenker's measurements might lower the experimental curve. If, however, the difference is real, it would mean that there are additional repulsive forces at play between the ion and the surface, besides the Coulomb image force. In the present stage of theory and experiment, all that can be done is to estimate limits for the possible magnitude and range of these additional forces.

The Coulomb image force, whose potential is inversely proportional to the first power of the distance, represents an ion-dipole attraction. The possible corrections would involve quadrupole and second order dipole effects, etc., so that their potential ought to decrease at least as the third power of the distance. Repulsive forces of this type would practically exclude all ions within their effective range, which is then the only important measure of the forces. A comparison between Figs. 2 and 3 shows immediately the effect to be expected from forces at a given range.

Thus interpreted, the available data on the surface tensions of uni-univalent electrolytes indicate that Coulomb's law is valid for distances greater than a molecular diameter (3×10^{-8} cm) from the surface.

[11] Schwenker, Ann. d. Physik **11**, 525 (1931).

On the Theory of Flame Propagation[1]

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A new theory of flame propagation in slow inflammation is proposed which considers that the highly energized atoms or radicals formed in the flame front play a more important rôle than heat conductivity in bringing the unburned gas to the reacting state. A small number of atoms or radicals diffuse over into the unburned phase, there initiating the chemical reaction. This and other considerations allow one to propose that the sum of thermal and chemical energy per unit mass of gas in all layers from the burned phase to the unburned phase is constant. The fundamental equation for the velocity V of the flame is derived simply from the fact that the number of molecules of combustible gas entering the reaction zone (flame front) in unit time equals the number reacting in the zone in the same time. If the flame front extends from x_u to x_b and the unburned gas enters it at a rate just sufficient to maintain the flame front stationary, then for 1 $\overline{\text{cm}}^2$ cross section the equation reads:

$$VN_{c(u)} = \int_{Tu}^{Tb} -\frac{\partial N_c}{\partial t}\frac{dx}{dT}dT$$

where V is the flame speed which is identical with the volume of unburned gaseous mixture (under initial conditions) entering the reaction zone per sec.; $N_{c(u)}$ is the concentration of combustible gas in molecules/cc in the unburned phase; and T_b and T_u are temperatures of the completely burned and unburned gases at x_b and x_u, respectively. This equation, in addition to the postulates that the sum of thermal and chemical energy per unit mass remains constant and that the rate of change of concentration of the various gas constituents in an elementary layer due to mass flow, diffusion and chemical reaction is zero, allows a solution of the problem. The theory is applied to explosions of mixtures of ozone gas and oxygen. Ozone decomposes to oxygen, with evolution of heat. With the help of the postulate that the total energy per unit mass is constant, the terms $\partial N_c/\partial t$ and dx/dT can be expressed as functions of temperature alone, and the above equation can be solved. In view of certain simplifications the calculated velocities are considered to be in satisfactory agreement with the experimental velocities. *The theory furnishes knowledge of the structure of the flame front.* A particular explosion is analyzed. The width of its flame front is shown to be about 10^{-3} cm. The temperature distribution, the distribution of the concentrations of various molecular and atomic species, and the rate of reaction throughout the flame front are given. The authors add an appendix, which includes a critical analysis of the essential differences between the present theory and previous theories of other investigators.

THERE are two general types of flame movement through mixtures of combustible gases. One is known as slow combustion or inflammation and moves with speeds of the order 10^2 to 10^3 cm per second, while the other is the phenomenon of the detonation wave, which travels with speeds of the order 10^5 cm per second. Treatments of the latter which account for the high velocities are to be found in the hydrodynamic theory of Chapman[4] and Jouguet,[5] and the chain-reaction theory of Lewis.[6]

The phenomenon of inflammation, with which the present paper is concerned, has been treated by several investigators[7] on the assumption that before any reaction occurs the unburned gas preceding the flame front is raised to its "*ignition temperature*" by heat conduction from the burning gases. In the light of modern chemistry we believe this conception is inadequate, since it omits all consideration of the rôle played by the active atoms and radicals known to exist in the flame front. It is quite conceivable that flame

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[4] Chapman, Phil. Mag. **47**, 90 (1899).

[5] Jouguet, J. de Mathématique 347 (1905); 6 (1906). *Mécanique des Explosifs*, Paris, 1917.

[6] Lewis, J. Am. Chem. Soc. **52**, 3120 (1930).

[7] Mallard and LeChatelier, Ann. de Mines **4**, 274 (1883). (See also Mason and Wheeler, J. Chem. Soc. (London) **111**, 1044 (1917).)

Jouguet, Compt. Rend. **156**, 872 (1913); **179**, 454 (1924); *Mécanique des Explosifs*, Paris, 1917.

Jouguet and Crussard, ibid. **168**, 820 (1919).

Nusselt, Z. des Vereins Deutscher Ingenieure **59**, 872 (1915).

Daniell, Proc. Roy. Soc. **A126**, 393 (1930).

propagation is governed by diffusion of these active radicals into the unburned mixture, which gives rise to chemical reaction there in a far more efficient way than would be possible purely by heat transfer. An enormous amount of experimentation[8] in reaction kinetics, especially in recent years, has shown that chemical reaction can be initiated at ordinary temperatures by introducing a few active radicals into a gas which ordinarily would require the attainment of higher temperatures to initiate combustion. The question may therefore be raised as to the utility of the conception of ignition temperature in the neighborhood of the flame front, with its high concentration of active radicals.

By the earlier heat-conductivity theory, thermal energy is conducted into the layer of unburned gas which already contains its original thermal plus chemical energy per unit mass. This introduces an energy "hump" into the unburned phase adjacent to the flame front.

The theory of flame propagation outlined in this paper allows one to conceive that reaction is initiated in the unburned phase by a relatively small number of active atoms or radicals and that the reaction is initiated faster than could be accomplished by heat transfer in a similar period of time. In this way, the energy "hump" reduces to a minimum and tends to disappear. This leads us to the working hypothesis of the present theory, namely, that the sum of thermal and chemical energy per unit mass in any elementary layer between the unburned and the burned phases remains sensibly constant. This is a very useful relationship. Since the thermal energy per unit mass in any elementary layer is determined by the existing temperature, the corresponding available chemical energy per unit mass in the same layer is fixed and may also be expressed as a function of thermal data alone. Since the chemical energy depends upon the concentration of the reactive gases the concentration distribution throughout the reaction zone is determined by the temperature gradient dT/dx. The latter, therefore, remains the only independent variable along the x axis.

[8] For example, the phenomenon of photo-explosions at ordinary or slightly elevated temperatures and the effect of the introduction of atoms and other reactive species into combustible mixtures.

Development of Equations and Application to Explosions in Gaseous Ozone-Oxygen Mixtures

We have developed equations which conform to the conception outlined above and have applied them to the calculation of flame speeds in mixtures of ozone and oxygen for which experimental data are available.[9]

Mixtures of gaseous ozone with inert gases explode when ignited. The resulting flame travels with a definite speed, depending upon the conditions of composition, temperature, and pressure. Such explosions are especially suitable for testing the theory because the net chemical reaction involved is of the simplest type possible in nature, namely,

$$O_3(\text{gas}) = 1\tfrac{1}{2}O_2 + 34{,}220 \text{ calories.}$$

One has no direct knowledge of the intermediate chain mechanism of the reaction. However, the possibilities are very few, and there is rather general agreement among recent investigators that the chief reactions involved are

(a) $O_3 \rightleftharpoons O_2 + O$,

(b) $O + O_3 = 2O_2$.

The relation for the velocity of the flame is derived simply from the fact that the number of molecules of ozone gas entering the reaction zone per unit time equals the number of molecules of ozone reacting in unit time in this zone. The width of the zone extends from xu to xb. The unburned gas enters the zone at the point xu (this direction being positive) with such velocity that the flame front remains stationary. Consider a cross section of 1 $\overline{\text{cm}}^2$; then, since $1O_3$ gives rise to $1.5O_2$,

$$VN_{O_3}(u) = \int_{xu}^{xb} \frac{1}{1.5}\left(\frac{\partial N_{O_2}}{\partial t}\right)_c dx, \qquad (1a)$$

where V is the flame speed sought, which is identical with the volume of unburned gaseous mixture (under initial conditions) entering the reaction zone per sec. at point xu.

$N_{O_3}(u)$ is the initial ozone concentration, in

[9] Lewis and von Elbe, J. Chem. Phys. **2**, 283 (1934).

molecules per cc, at the temperature Tu and pressure of the unburned gas.

$(\partial N_{O_2}/\partial t)_c$ is the rate of formation of oxygen in molecules per cc per sec.

The integral is taken over all elementary volumes dx.

In general, subscripts u and b denote unburned and burned states, respectively.

Since the temperature rises from Tu at xu to the final temperature Tb at xb Eq. (1a) may be rewritten:

$$VN_{O_3}(u)=\int_{Tu}^{Tb}\frac{1}{1.5}\left(\frac{\partial N_{O_2}}{\partial t}\right)_c\frac{dx}{dT}dT. \quad (1)$$

Obviously, $(\partial N_{O_2}/\partial t)_c$ and dx/dT are functions of the concentrations of O_2, O and O_3, and now the task is to express both these terms as functions of temperature alone.

To maintain a steady state, the rate of change of concentration of each component in an elementary layer at any point x must be zero. The concentration of each component is determined by the mass flow, diffusion and chemical reaction in the elementary layer. In the following, the indices V, D and c denote mass flow, diffusion, and chemical reaction, respectively, of the three components O_2, O and O_3.

The following three equations may therefore be written:

$$\left(\frac{\partial N_{O_2}}{\partial t}\right)_V+\left(\frac{\partial N_{O_2}}{\partial t}\right)_D+\left(\frac{\partial N_{O_2}}{\partial t}\right)_c=0 \quad (2)$$

$$\left(\frac{\partial N_O}{\partial t}\right)_V+\left(\frac{\partial N_O}{\partial t}\right)_D+\left(\frac{\partial N_O}{\partial t}\right)_c=0 \quad (3)$$

$$\left(\frac{\partial N_{O_3}}{\partial t}\right)_V+\left(\frac{\partial N_{O_3}}{\partial t}\right)_D+\left(\frac{\partial N_{O_3}}{\partial t}\right)_c=0. \quad (4)$$

The first terms of Eqs. (2), (3) and (4) are functions of concentration and Vx, where Vx is a volume of gas pushed through the layer at x in unit time by mass flow in the direction of the burned phase. Obviously, for xu, Vx becomes V in Eq. (1). The second terms in Eqs. (2), (3) and (4) are functions of the concentration gradient and Dx, where Dx is the diffusion coefficient corresponding to the layer at x.

Eqs. (1) to (4) contain, therefore, six variables dx/dT, Vx, Dx, N_{O_2}, N_{O_3}, and N_O. To express Eq. (1) as a function of temperature alone, two more equations are required.

The fifth equation is given by the gas law:

$$N_{O_2}+N_{O_3}+N_O=N_{O_2}(b)Tb/T \quad (5)$$

where $N_{O_2}(b)$ is the number of oxygen molecules in 1 cc at the end of the reaction zone, namely, where $T=Tb$. Thermal dissociation of oxygen in the completely burned gas is neglected, and therefore the burned phase consists of oxygen molecules only.

The sixth equation is derived from the fundamental hypothesis that the total thermal and chemical energy per unit mass in any elementary layer is constant. (See Appendix for further discussion.) It follows that the chemical energy still available in any layer at temperature T would be just sufficient, if released, to raise the temperature of the gases in the layer from T to Tb. Thus,

$$E_{O_3T}N_{O_3}+E_{OT}N_O=(N_{O_2}+1.5N_{O_3}+0.5N_O)C_{p_T}{}^{Tb}(Tb-T) \quad (6)$$

where $C_{p_T}{}^{Tb}$ is the mean molar heat capacity of O_2 at constant pressure between the temperatures indicated; E_{O_3T} is the heat of decomposition of 1 mol of ozone at the temperature T, and E_{OT} is the heat of recombination of 1 mol of oxygen atoms at the temperature T.

We shall not attempt an exact solution of the above six equations. In the first place, we have no knowledge of the problem of diffusion of three gases into each other; and, in the second place, information regarding the rate of reversible reaction (a) is not available. We propose to approximate the entire solution by introducing certain simplifications. In the diffusion term of Eq. (2) we shall employ the following equation for the diffusion coefficient D

$$D=\Omega_{O_2}\lambda_{O_2}/3, \quad (7)$$

where Ω_{O_2} is the average velocity of the oxygen molecules at temperature T, and λ_{O_2} is the mean free path in a gas consisting of oxygen molecules. We believe this approximation introduces only secondary changes in the final result.

Furthermore, the third terms in Eqs. (2), (3) and (4) and also the term $(\partial N_{O_2}/\partial t)_c$ in Eq. (1) are really each composed of three parts. The first and second parts represent the rates of the reversible reaction (a) and the third part the

rate of the reaction (b). As mentioned above, no kinetic data are available for the first two parts, while the third part can be evaluated easily from the collision frequency and the heat of activation. To dissolve this difficulty, we shall assume that the equilibrium represented by Eq. (a) exists throughout the reaction zone. It is realized that this condition is not fulfilled at lower temperatures near the unburned side of the flame front, but as the temperature increases toward the burned side it approximates actual conditions more and more. The assumption becomes more nearly true for the higher temperature explosions. This approximation, which will tend to increase the calculated flame speeds, introduces perhaps the most serious error into the calculations and will receive further discussion later.

By introducing Eq. (7) for the diffusion coefficient and the condition of equilibrium, namely,

$$K_c = N_O N_{O_2}/N_{O_3}, \tag{8}$$

one may dispense with Eqs. (3) and (4). K_c is the equilibrium constant when the concentrations are measured in molecules per cc.

Using Tolman's[10] numerical factor for Ω_{O_2} and placing $\sigma_{O_2}=3\times10^{-8}$ cm, one obtains

$$D=\frac{14{,}500T^{\frac{1}{2}}(1/M_{O_2})^{\frac{1}{2}}\times0.707}{3\pi\times(3\times10^{-8})^2\times N_{O_2}(b)Tb/T}, \tag{9}$$

$$N_{O_2}(b)=2.71\times10^{19}(273/Tb)(P/760), \tag{10}$$

where P is the total pressure in mm Hg.

$$N_{O_2}(b)Tb/T=2.71\times10^{19}(273/T)(P/760) \tag{11}$$

and

$$D=\frac{2.2\times10^{-2}T^{\frac{1}{2}}}{P}. \tag{12}$$

K_c is evaluated as follows:

$$K_p=\frac{p_O p_{O_2}}{p_{O_3}}, \tag{13}$$

where p_O, p_{O_2}, and p_{O_3} are the partial pressures of the constituent gases.

Since

$$p_O=\frac{P N_O}{N_{O_2}(b)Tb/T};\quad p_{O_2}=\frac{P N_{O_2}}{N_{O_2}(b)Tb/T};$$

$$p_{O_3}=\frac{P N_{O_3}}{N_{O_2}(b)Tb/T} \tag{14}$$

$$K_c=(K_p/P)N_{O_2}(b)Tb/T. \tag{15}$$

Furthermore, $\log K_p$ obeys the equation

$$\log K_p=-\Delta H_T/4.573T+\text{constant}, \tag{16}$$

where ΔH_T is the heat of the reaction $O+O_2=O_3$ at temperature T and constant pressure and has a mean numerical value of 24,400 calories. From the data of Kassel,[11] the constant is 9.48 if P is measured in mm Hg.

Therefore

$$K_c=3.03\times10^9\frac{N_{O_2}(b)}{P}\frac{Tb}{T}e^{-12{,}300/T}. \tag{17}$$

Eqs. (5), (6) and (8) may be used to express the concentrations of O, O_2, and O_3 as functions of temperature.

From Eq. (5)

$$N_{O_2}=N_{O_2}(b)\frac{Tb}{T}-N_{O_3}-N_O. \tag{18}$$

The calculations will be simplified enormously by making

$$N_{O_2}\backsimeq N_{O_2}(b)Tb/T. \tag{19}$$

This approximation can be made without serious error, especially at intermediate and higher temperatures, because the concentrations of O_3 and O, which are required to fulfill Eq. (6), become very small. It should be mentioned also in this connection that the experiments with which the calculated flame speeds will be compared were made with mixtures especially rich in oxygen.

By combining Eqs. (6) and (8) and using the simplified symbol C_p for $C_{p_T{}^{T_b}}$,

$$N_{O_3}=\frac{N_{O_2}+1.5N_{O_3}+0.5N_O}{(K_c/N_{O_2})E_{O_T}+E_{O_{3T}}}C_p(Tb-T), \tag{20}$$

which from Eq. (19) resolves to

$$N_{O_3}=\frac{N_{O_2}(b)(Tb/T)C_p(Tb-T)}{K_cE_{O_T}/N_{O_2}(b)(Tb/T)+E_{O_{3T}}}. \tag{21}$$

[10] Tolman, *Statistical Mechanics*, p. 63, Eq. (95), 1927.

[11] Kassel, J. Chem. Phys. **1**, 414 (1933).

By combining Eq. (21) with (8) and (19)

$$No=\frac{KcCp(Tb-T)}{KcEo_T/No_2(b)(Tb/T)+Eo_{3T}}. \quad (22)$$

EVALUATION OF dx/dT

dx/dT will be evaluated by a consideration and development of Eq. (2), which may be written:

$$-\frac{\partial}{\partial x}(No_2V_x)dx+\frac{\partial}{\partial x}D\left(\frac{\partial No_2}{\partial x}\right)dx+\left(\frac{\partial No_2}{\partial t}\right)_c dx=0, \quad (23)$$

where dx is the thickness of the elementary layer of 1 $\overline{cm}^2$ cross section.

Since the mixture becomes richer in oxygen molecules in the direction unburned phase to burned phase, more oxygen molecules are pushed out of the layer than are pushed in by mass flow. The first term is therefore negative. Since chemical reaction leads to formation of oxygen molecules the third term is positive. Since the O_2 concentration decreases with increasing temperature (Eq. 19) and the positive direction of the x-axis is the direction of increasing temperature, the sign of the diffusion term is positive.

Then

$$-V_x\frac{\partial No_2}{\partial x}-No_2\frac{\partial V_x}{\partial x}+\frac{\partial}{\partial x}\left(D\frac{\partial No_2}{\partial x}\right)+\left(\frac{\partial No_2}{\partial t}\right)_c=0. \quad (24)$$

If we let $w=\partial T/\partial x$ this may be written as,

$$-wV_x\frac{\partial No_2}{\partial T}-wNo_2\frac{\partial V_x}{\partial T}+w\frac{\partial}{\partial T}\left(wD\frac{\partial No_2}{\partial T}\right)+\left(\frac{\partial No_2}{\partial t}\right)_c=0. \quad (25)$$

Using Eq. (19) and substituting $\partial No_2/\partial T$ and No_2 in Eq. (26) and dividing by $No_2(b)Tb$ we obtain

$$+\frac{wV_x}{T^2}-\frac{w}{T}\frac{\partial V_x}{\partial T}-w\frac{\partial}{\partial T}\left(\frac{wD}{T^2}\right)+\frac{1}{No_2(b)Tb}\left(\frac{\partial No_2}{\partial t}\right)_c=0. \quad (26)$$

Volumes Vx contain equal masses and therefore, strictly speaking,

$$V_x=\frac{VT}{Tu}\frac{1+0.5a+m}{1+m}, \quad (27)$$

where m is the ratio mols O_2/mols O_3 in the original mixture and $0\leqq a\leqq 1$. However, in line with the approximation made in Eq. (19), it is essentially correct, especially for intermediate and higher temperatures, to write

$$V_x\cong\text{const.}\times T. \quad (28)$$

Eq. (26) becomes,

$$-w\frac{\partial}{\partial T}\left(\frac{Dw}{T^2}\right)+\frac{1}{No_2(b)Tb}\left(\frac{\partial No_2}{\partial t}\right)_c=0. \quad (29)$$

As will be shown later, $(\partial No_2/\partial t)_c$ can be expressed as a function of temperature. Placing

$$\frac{1}{No_2(b)Tb}\left(\frac{\partial No_2}{\partial t}\right)_c=f(T),$$

$$-\frac{wD}{T^2}\frac{\partial}{\partial T}\left(\frac{wD}{T^2}\right)+\frac{D}{T^2}f(T)=0. \quad (30)$$

Let $wD/T^2=y$. Then,

$$-y\frac{\partial y}{\partial T}+\frac{D}{T^2}f(T)=-\frac{1}{2}\frac{\partial y^2}{\partial T}+\frac{D}{T^2}f(T)=0. \quad (31)$$

To integrate Eq. (31) it becomes necessary to introduce a limiting condition. We shall choose $w=0$ when $T=Tu$, an assumption which implies that there is no temperature discontinuity between the unburned phase and the reaction zone. Considering the mode of activation of the unburned gas this probably is not far from the truth. (See Appendix.) Then

$$y^2=\frac{D^2w^2}{T^4}=2\int_{Tu}^{T}\frac{D}{T^2}f(T)dT. \quad (32)$$

From Eq. (1)

$$V_{NO_3}(u)=\int_{Tu}^{Tb}\frac{1}{1.5}\left(\frac{\partial N_{O_2}}{\partial t}\right)_c dx$$

$$=\frac{1}{1.5}N_{O_2}(b)Tb\int_{Tu}^{Tb}(fT)\frac{dx}{dT}dT$$

$$=\frac{1}{1.5}N_{O_2}(b)Tb\int_{Tu}^{Tb}\frac{f(T)dT}{w}. \quad (33)$$

Then

$$\frac{1.5V_{NO_3}(u)}{N_{O_2}(b)Tb}=\int_{Tu}^{Tb}\frac{f(T)dT}{w} \quad (34)$$

$$=\int_{Tu}^{Tb}\frac{\frac{D}{T^2}f(T)dT}{\left(2\int_{Tu}^{T}\frac{D}{T^2}f(T)dT\right)^{\frac{1}{2}}} \quad (35)$$

$$=\left(2\int_{Tu}^{T}\frac{D}{T^2}f(T)dT\right)^{\frac{1}{2}}\Bigg|_{Tu}^{Tb} \quad (36)$$

$$=\sqrt{2}\left(\int_{Tu}^{Tb}\frac{D}{T^2}f(T)dT\right)^{\frac{1}{2}} \quad (37)$$

$$=\sqrt{2}\left(\frac{1}{N_{O_2}(b)Tb}\int_{Tu}^{Tb}\frac{D}{T^2}\left(\frac{\partial N_{O_2}}{\partial t}\right)_c dT\right)^{\frac{1}{2}}. \quad (38)$$

Since

$$N_{O_3}(u)=\frac{N_{O_2}(b)}{1+m}\frac{Tb}{Tu}. \quad (39)$$

Eq. (38) becomes

$$V=\frac{1.41(1+m)Tu}{1.5(N_{O_2}(b)Tb)^{\frac{1}{2}}}\left(\int_{Tu}^{Tb}\frac{D}{T^2}\left(\frac{\partial N_{O_2}}{\partial t}\right)_c dT\right)^{\frac{1}{2}}. \quad (40)$$

$(\partial N_{O_2}/\partial t)_c$ is evaluated as follows. As mentioned above, only reaction (b) will be considered because of the assumption of equilibrium by reaction (a). The rate of reaction (b) is determined by the collision frequency between oxygen atoms and ozone molecules and by the probability that reaction will take place on collision. The number of collisions per sec. per cc between O and O_3 is given by the expression.[12]

$$Z=2N_O N_{O_3}(\sigma_{O,O_3})^2\left(2\pi RT\frac{M_O+M_{O_3}}{M_O M_{O_3}}\right)^{\frac{1}{2}}, \quad (41)$$

where R is the gas constant, and M_O and M_{O_3} are the molecular weights of the oxygen atom and the ozone molecule, respectively.

The probability that reaction (b) takes place, or the ratio of the number of successful collisions to the total number of collisions is given by the expression $ke^{-E/RT}$, where E is the energy of activation. In the simpler bimolecular reactions k is of the order unity. An accurate value of E is not known, but the best available value[13] seems to be about 6000 calories per mol.

Every successful collision produces 2 molecules of oxygen, and therefore

$$(\partial N_{O_2}/\partial t)_c=2Ze^{-E/RT}. \quad (42)$$

Introducing the expressions for N_{O_3} and N_O of Eqs. (21) and (22) in the expression for Z, and substituting Eq. (42) and D of Eq. (12) in Eq. (40), one obtains:

$$V=\frac{1.41(1+m)Tu}{1.5(N_{O_2}(b)Tb)^{\frac{1}{2}}}\times\left(\int_{Tu}^{Tb}\frac{2.2\times10^{-2}}{PT}\times\frac{4K_c(C_p)^2(Tb-T)^2N_{O_2}(b)Tb}{(K_cE_{O_T}/N_{O_2}(b)(Tb/T)+E_{O_{3T}})^2}e^{-6000/RT}\times(\sigma_{O,O_3})^2\sqrt{2\pi R\frac{M_O+M_{O_3}}{M_O M_{O_3}}dT}\right)^{\frac{1}{2}} \quad (43)$$

With the following numerical values $E_{O_T}=58{,}000$ calories/mol; $E_{O_{3T}}=34{,}000$ calories/mol; $M_O=16$; $M_{O_3}=48$; $\sigma_{O,O_3}=3\times10^{-8}$ cm; and substituting the value of K_c in Eq. (17) and combining the numerical factors one obtains:

$$V=1.05\times10^8C_p(1+m)TuP^{\frac{1}{2}}\left(\int_{Tu}^{Tb}\frac{[(Tb/T)-1]^2e^{-15{,}300/T}}{(1.76\times10^{14}e^{-12{,}300/T}+3.4\times10^4P)^2}dT\right)^{\frac{1}{2}}, \text{ cm/sec.}, \quad (44)$$

[12] Tolman, *Statistical Mechanics*, p. 242, 1927.

[13] O. R. Wulf, J. Am. Chem. Soc. **54**, 156 (1932); H. J. Schumacher, ibid. **52**, 2377 (1930).

w may be determined from Eq. (32).

$$\frac{D^2w^2}{T^4}=\frac{2}{N_{O_2}(b)Tb}\int_{Tu}^{T}\frac{D}{T^2}\left(\frac{\partial N_{O_2}}{\partial t}\right)_c dT \tag{45}$$

$$=2.48\times10^{16}(Cp)^2P\int_{Tu}^{T}\frac{[(Tb/T)-1]^2e^{-15,300/T}}{(1.76\times10^{14}e^{-12,300/T}+3.4\times10^4P)^2}dT \tag{46}$$

$$w=7.17\times10^9CpP^{\frac{1}{2}}T^{\frac{1}{2}}\left(\int_{Tu}^{T}\frac{[(Tb/T)-1]^2e^{-15,300/T}}{(1.76\times10^{14}e^{-12,300/T}+3.4\times10^4P)^2}dT\right)^{\frac{1}{2}}\text{ deg./cm.} \tag{47}$$

The reaction rate is determined from Eq. (42) by using the numerical factors of the above equations.

$$\left(\frac{\partial N_{O_2}}{\partial t}\right)_c=5.52\times10^{36}(Cp)^2P^3T^{\frac{1}{2}}\frac{[(Tb/T)-1]^2e^{-15,300/T}}{(1.76\times10^{14}e^{-12,300/T}+3.4\times10^4P)^2}\text{molecules } O_2/\text{sec. cc.} \tag{48}$$

Numerical values of speeds of flames were determined for specific explosions by graphical integration. The calculation has been carried out for several experiments, and the results are given in Table I.

TABLE I.

Experiment	P, mm Hg	Tu, °K	Tb, °K	m	V, cm/sec. exptl.	V, cm/sec. calc.
3.13	624	300	1239	3.054	55	253
3.13	2560	427	1343	3.054	158	451
3.32	495	302	1922	1.016	160	333
3.32	3760	468	2044	1.016	747	664

It will be recalled that certain approximations and assumptions had to be made, either because of insufficient available knowledge of the details of the reaction or because of mathematical complexities. The assumption that reaction (a) reaches equilibrium results in calculated values which are too large. In reality, equilibrium is not approached, except perhaps at high temperatures. The oxygen atoms which diffuse over into the colder side of the reaction zone do not disappear there as fast as they would if equilibrium were established. The reaction, therefore, actually goes slower than the assumption of equilibrium would predict. This effect would be more pronounced for lower than for higher initial temperatures. For this reason, one should expect a gradual improvement in the differences between the observed and calculated speeds as the temperature increases. It is noteworthy that in the higher temperature region where, because of approximations, the theory is expected to apply best in this particular reaction, the observed and calculated speeds do approach one another.

We wish to emphasize that, although the theory proposed may be essentially correct, its universal application, even in the seemingly simple present case, is hampered by lack of quantitative knowledge of the reactions involved.

STRUCTURE OF FLAME FRONT

The structure of the reaction zone has been worked out for experiment 3.32 and is presented in Fig. 1. It contains the temperature, the concentrations of oxygen atoms and ozone molecules, and the rate of chemical reaction plotted against the distance from the Tb side of the reaction zone. Toward the unburned side the temperature drops very slowly to Tu because the atom concentration and therefore the rate of reaction is too small on account of the necessity for neglecting the atom diffusion. Therefore it is practical to measure distances from the Tb side and to extend the curve toward the Tu side only to the point at which the reaction becomes very small. The width of the reaction zone for this explosion is of the order 10^{-3} cm.

The curve T *versus* x is obtained by first integrating Eq. (47) graphically, plotting $1/w=dx/dT$ against T and again integrating graphically.

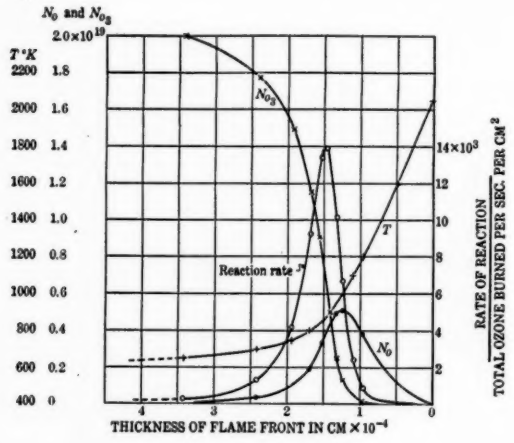

FIG. 1. Structure of flame front: showing temperature gradient, distribution of ozone and oxygen atoms and the reaction rate throughout the flame front. Experiment 3:32—pressure = 3760 mm Hg, $T_u = 468°K$, $T_b = 2044°K$, $m = 1.016$.

Instead of plotting $(\partial N_{O_2}/\partial t)_c$ *versus* x, we plot the expression $(1/1.5)(\partial N_{O_2}/\partial t)_c(1/VN_{O_3}(u))$, which is proportional to it. The total area under this curve is unity. Any fraction of this area represents the percentage reaction occurring up to point x. At the same time, the curve provides a measure of the rate of reaction at any point, x.

The equations for N_{O_3} and N_O are

$$N_{O_3} = \frac{1.215\times10^{27}[(T_b/T)-1]}{1.76\times10^{14}e^{-12,300/T}+1.28\times10^{8}}, \tag{49}$$

$$N_O = \frac{9.78\times10^{32}e^{-12,300/T}[(T_b/T)-1]}{1.76\times10^{14}e^{-12,300/T}+1.28\times10^{8}}. \tag{50}$$

Incidentally it should be remarked that the three-body collision reaction $O+O+O_2=2O_2$ which has not been mentioned, is negligible compared with the reaction $O+O_3=2O_2$ except in the last portions of the reaction zone. Here, however, its contribution to the speed is inappreciable because most of the reaction is complete.

The slower temperature rise in the first part of the zone compared with the more rapid rise in the last part is due to the preponderance in the first part of the endothermic reaction $O_3=O_2+O$ and the preponderance in the last part of the highly exothermic atom recombination.

ACKNOWLEDGMENT

It is a pleasure to thank Dr. Morris Muskat of the Gulf Research Laboratory for the opportunity of discussing several mathematical points with him and Professor R. C. Tolman for reading the manuscript in its final form.

APPENDIX

The authors feel that the present paper would be incomplete without a critical analysis of the essential differences between the theory herein proposed and previous theories.

To begin with it is to be noted that the theories of Jouguet, Nusselt, and Daniell[7] are fundamentally identical. In the first place, a relationship is introduced explicitly or implicitly which is essentially identical with our Eq. (1). Secondly, since the reaction zone is assumed to be stationary, a relationship is used which states that the rate of change of heat energy in an elementary layer dx due to conduction, mass flow, and chemical reaction equals zero. This equation may be written in the following way, if cooling losses are neglected:

$$k\frac{d^2T}{dx^2}-cm\frac{dT}{dx}+\left(\frac{dH}{dt}\right)_{\text{chem.}}=0,$$

where k is the coefficient of heat conductivity,
m is the mass passing unit area in the time element dt,
c is the specific heat per unit mass,
$(dH/dt)_{\text{chem.}}$ represents the rate of liberation of thermal energy due to chemical reaction within the elementary layer dx.

Both relationships allow complete solution of the problem, provided an assumption is made regarding the progress of the chemical reaction along the x axis, that is, the percentage of the original chemical energy which has been spent up to the point x. Daniell leaves the latter in a general term, dn/du, in his fundamental equation[14] and he shows that by introducing any desirable assumption regarding the progress of the reaction, a solution may be obtained. His equation, moreover, contains another general term, λ, which by his equations (6) and (9) is a

[14] Reference 7, Eq. (15), page 398.

function of the reaction rate in the usual purely kinetic sense. Nusselt, studying flame propagation in hydrogen-air mixtures, arbitrarily assumes that equal amounts of heat energy are released in unit lengths of the x axis. Furthermore, he assumes a kinetic reaction-rate equation which we now know to be erroneous. By introducing an empirical constant, qualitative agreement is found with experiment, but this may not be accepted as proof for the validity of the underlying conceptions. Jouguet obtains the same fundamental formula[15] as Daniell, but it already includes specific assumptions regarding both the progress of the reaction along the x axis and the kinetic rate of chemical reaction. These assumptions are embodied in the formulae (written in Jouguet's symbols)

$$d\alpha/dt = u\,d\alpha/dx,$$

$$d\alpha/dt = f(T, \alpha),$$

where u is the mass velocity at the point x, α is the fraction of chemical energy which is spent up to the point x, $f(T, \alpha)$ is the rate of chemical reaction in the kinetic sense.

Both the latter equations, taken together, mean that during the time element dt an elementary mass of gas moves a distance dx and an amount of chemical energy corresponding to $d\alpha$ is lost by chemical reaction. It should be noted that in Jouguet's (also Daniell's) conception no allowance is made for the possible flow of chemical energy by diffusion. The underlying physical picture of their conception, therefore, would seem to be that of an elementary mass of gas moving along the x axis, through which the process of heat conduction may take place, but not intermixing by diffusion with neighboring mass elements. Both equations allow a solution for $d\alpha/dx$ (the latter is identical with Daniell's dn/du) in terms of reaction rate and mass velocity.

In our treatment, aside from dismissing the concept of ignition temperature, for reaction may be initiated by active radicals at practically initial temperature, we postulate that the rate of change of *concentration* of the various gas constituents in an elementary layer, due to mass flow, diffusion, and chemical reaction, is zero. The problem of the progress of the reaction along the x axis is solved by introducing a new working hypothesis, namely, the energy relationship expressed in Eq. (6), which states that the total energy, thermal plus chemical, per unit mass in any elementary layer along the x axis is constant. We believe that this hypothesis, while speculative in character, is more defensible than either of those of Jouguet or Nusselt.

The assumption that flame propagation is determined by heat conductivity and ignition temperature involves the establishment of an energy "hump" in the unburned phase adjacent to the flame front. This must be so, since thermal energy is conducted into the layer of unburned gas which already contains its original thermal plus chemical energy per unit mass. Thus, while the sum of thermal and chemical energy per unit mass in an incompletely burned layer may exceed the total thermal energy per unit mass in the completely burned gas it cannot fall below the value for the completely burned gas if the flame front is to be stable. This can be understood from the following consideration. Suppose a layer in the flame front which is not yet completely burned (near the burned side of the flame front) contains such an amount of energy that the residual chemical energy is insufficient to raise the mass of gas to the final temperature of the completely burned gas. Then energy must flow into this layer if it is to reach the final temperature. In view of the rising temperature gradient from the unburned to the burned phase, thermal energy can flow into it only from the direction of completely burned gas. Since the chemical energy of the latter is spent, such a process would result in a decrease of its own temperature; that is, an energy "valley" of this sort would correspond to an unstable state in the flame front. It follows that the energy per unit mass of the completely burned phase represents the minimum total energy, chemical and thermal, which may be possessed by any unit mass of gas in the reaction zone.

Eq. (6) is therefore the lower limit of the general relationship

$$E_{O_3 T} N_{O_3} + E_{O_T} N_O \geqq (N_{O_2} + 1.5 N_{O_3} + 0.5 N_O) C_{p_T}{}^{T_b} (T_b - T)$$

[15] Jouguet, Compt. Rend. **179** (1924), Eq. 4, page 456. Priority belongs to Jouguet.

and therefore possesses definite physical significance. As a matter of fact, we may conceive of Eq. (6) representing rather closely the true conditions, as outlined early in this paper. Eq. (6), with the condition that the rate of change of concentrations in an elementary layer is zero, automatically takes care of the requirement that the rate of change of heat energy shall also be zero. The equations, however, go further in that they also impose conditions as to the flow of chemical energy among the different layers which, as pointed out, the other theories neglect.

In common with other authors our differential equation is solved by imposing a condition regarding the temperature gradient. The type of our equation is such that its solution is imaginary if one assumes that the temperature gradient disappears at point x_b where the gas is completely burned. The solution is obtained by making the temperature gradient disappear toward the unburned side. We believe that this is in harmony with the physical picture of the theory. In their equations, Jouguet and Nusselt impose the condition that the temperature gradient disappears toward the burned side, although for mathematical purposes the same condition may be employed for the unburned side. The latter was utilized by Daniell.

The Electric Moments of Fatty Acids

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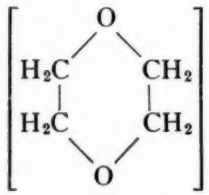
(Received May 23, 1934)

A number of investigators have reported moments of fatty acids from dielectric constant and density measurements made upon the solutions of these substances in benzene. As is well known, fatty acids exist as double molecules when dissolved in hydrocarbons and consequently these reported moments have no significance as applied to the single molecules. No detailed reference to this work need be given. From measurements made upon the gaseous substances Zahn[1] reported moments of 1.51−, 1.73− and 1.74×10^{-18} c.g.s.e.s.u. for the simple molecules of formic, acetic and propionic acids, respectively. At the temperatures of measurement the formic acid existed as a mixture of single and double molecules. From a knowledge of the density of the gas the fraction of the molecules in the associated state was calculated and the moments of both the single and double molecules were reported. The latter was given to be 0.99 D. The moments of acetic and propionic acids were obtained from measurements made at temperatures sufficiently high that dissociation of the double molecules into single molecules was sufficiently complete.

Oxygenated solvents have the property of dissociating the double fatty acid molecules into single ones. Nearly all of the common oxygenated solvents are polar and therefore not suited as media for measuring the moments of polar solutes. Recently dioxane



has been used in the determination of electric moments. It is non-polar and miscible with the lower acids and dissolves sufficient amounts of the higher members. The authors measured the moments of formic, acetic and propionic acids in dioxane for the sake of making comparisons with the values obtained for the gaseous substances. In order to determine the effect of greatly increasing the length of the hydrocarbon chain data are also given for stearic acid in Table I.

The polarizations at infinite dilution were calculated by the method of Hedestrand.[2] In Table II are listed the values of the polarization at infinite dilution, the molecular refraction for the sodium line and the electric moment.

The moments of acetic and propionic acids as

[1] C. T. Zahn, Phys. Rev. **37**, 1516 (1931).

[2] Hedestrand, Zeits. f. physik. Chemie **B2**, 428 (1929).

TABLE I. *Dielectric constants and densities of solutions of fatty acids in dioxane.*
(Temp. 25°C.)

c_2	ϵ	d
	Formic acid	
0.000000	2.2357	1.02771
.017432	2.3409	1.02892
.026661	2.3968	1.02969
.036226	2.4503	1.03014
	Acetic acid	
0.000000	2.2357	1.02771
.021864	2.3258	1.02817
.026648	2.3443	1.02839
.034211	2.3740	1.02847
	Propionic acid	
0.000000	2.2357	1.02771
.028550	2.3534	1.02714
.031317	2.3649	1.02715
.036956	2.3898	1.02706
	Stearic acid	
0.000000	2.2357	1.02771
.009281	2.2713	1.02203
.014773	2.2927	1.01843
.017352	2.3005	1.01699

determined in dioxane are practically identical with those reported for the gaseous state. It will also be noted that lengthening the hydrocarbon chain has no effect on the moment of the fatty acid, the moment of stearic acid being identical with that of acetic acid. There is a considerable discrepancy between the values of the moment of formic acid obtained from measurements in dioxane and that calculated for the single molecules in the gaseous state. In order to check the work a second lot of C.P. formic acid was purchased and, as was done for acetic and propionic acids, purified by fractional crystallization followed by distilling through an efficient column. The two samples of formic acid gave the same moment.

TABLE II. *Polarizations and moments of fatty acids.*

Fatty acid	P_∞	MR_D	$10^{18}\,u$
Formic	90.52	8.56	2.07
Acetic	75.91	13.00	1.74
Propionic	80.78	17.50	1.75
Stearic	149.90	86.89	1.74

Apparently the replacement of hydrogen of formic acid by an alkyl group results in a considerable reduction of the moment. The steric effects and the inductive effects resulting from such a substitution are too complicated to be handled quantitatively at the present state of our knowledge.

The ionization constants at 25° of formic, acetic and propionic acids are $2.1(10^{-4})$, $1.8(10^{-5})$ and $1.4(10^{-5})$, respectively. Apparently the higher electric moment of formic acid is related to its higher ionization constant. It is possible that the O—H linkage is more polar in formic acid than it is in the higher fatty acids and this is suggested as a partial explanation of the considerable difference in moment of the first and later members of the series.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

The Exchange Reaction of Hydrogen and Deuterium Oxide

In the previous communication,[1] there is a typographical error in the expression for the distribution function (f_{H_2O}) for water. This expression should be multiplied by the statistical weight factor of 4. An additional error was called to our attention by Professor Urey through a private communication from Professor Bonhoeffer. The new calculated values for the equilibrium constant are in Table I. The agreement with the experiments at 525°C is good.

TABLE I. *Equilibrium constants for the reaction,* $HDO+H_2 \rightleftarrows H_2O+HD$.

T	300	400	500	600	700	800	900
k	0.35	0.51	0.60	0.68	0.74	0.79	0.83

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July 12, 1934.

[1] R. H. Crist, and G. A. Dalin, J. Chem. Phys. **2**, 442 (1934).

Is Water Isotopically Fractionated on Partial Condensation of Its Vapor? A Correction to My Paper on "The Natural Separation of Isotopes, etc."

Recently[1] I published an account of some experiments showing that the density of water obtained in the combustion of benzene, kerosene and honey is greater than that of ordinary water to the extent of several parts per million and concluded from these results that a natural separation of the isotopes of hydrogen had occurred. These results were of the same order of magnitude as the data published by Washburn and Smith on water obtained in the combustion of the combined hydrogen in a young willow tree,[2] but they did not agree with the data for water obtained by Washburn and Smith in the combustion of anthracite coal and natural propane. No excess density was found in these latter two cases.[3] Smith,[4] however, has discovered that the atomic weight of the tank oxygen used in the combustion of the willow tree was greater than that of ordinary oxygen; the difference being sufficient to bring the density of the water obtained in the combustion of the willow tree down to the density of the water obtained from the sap of the tree.

Since I burned the benzene and kerosene in dried air, the uncertainty of the atomic weight of tank oxygen does not enter into the interpretation of the data, but I have found another difficulty which indicates that although my density data are correct, an interpretation other than that of a natural separation of the isotopes of hydrogen must be given. It occurred to me that possibly an isotopic fractionation of water takes place in the act of partially condensing water from a rapidly moving stream of air. In order to answer this question I swept a rapid stream of air by a wick moistened with water at 90°C in an enclosed tube. The air then passed through a condenser where a fraction of the total water content of the air was condensed on cooling to the neighborhood of 17°C. The density of the condensed water was greater than that of ordinary water to the extent of 3.8 p.p.m. (average of three density measurements). This increase in density, due probably to an isotopic fractionation of water and not to impurities, is nearly sufficient to account for my observed results in the experiments in which the water was collected in a similar way; that is in the benzene and kerosene experiments. It is impossible to state definitely that this difficulty accounts for the entire increase in density observed due to the uncertainty concerning the total volume of air swept through the apparatus. I have, however, burnt benzene vapor by sweeping a comparatively slow stream of carbon dioxide over benzene at 65°C into a hand torch where the vapors being mixed with dry electrolytic oxygen a blue flame was produced. The water obtained from this combustion had identically the same density as ordinary water (within 0.3 p.p.m.). It thus appears that there is no *natural* separation of the isotopes of hydrogen, at least in the case of benzene.

I have also examined cholesterol from the spinal fluid of cattle and find a normal deuterium content.

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July 17, 1934.

[1] M. Dole, J. Chem. Phys. **2**, 337 (1934).
[2] E. W. Washburn and E. R. Smith, Science **79**, 188 (1934); Bur. Standards J. Research **12**, 305 (1934).
[3] E. W. Washburn and E. R. Smith, Bur. Standards J. Research **12**, 304 (1934).
[4] E. R. Smith, J. Chem. Phys. **2**, 298 (1934); Science **79**, 454 (1934).

Thermodynamic Properties of Steam at High Temperatures

In a recent paper[1] I computed the thermodynamic quantities for steam from the spectroscopic data of Mecke and his associates for temperatures up to 1500°K. The calculation was not extended above 1500° since some uncertainties in the data (more particularly the change in the rotational constants for the higher vibrational states) introduced for such temperatures appreciable errors in the calculated thermodynamic quantities. Since that time, however, I have received several requests for data for the range 1500°–3000°, and I have therefore extended the calculation. The results are given in Table I.

TABLE I.

T°K	$-(F°-E_0°)/T$ cal./deg.	$S°$ cal./deg.	$C°P$ cal./deg.	$H-E_0°$ kilocal.	$E-E_0°$ kilocal.
1500	50.59	59.78	11.15	13.80	10.82
1750	52.03	61.54	11.67	16.65	13.17
2000	53.32	63.13	12.09	19.62	15.65
2250	54.49	64.58	12.4	22.69	18.22
2500	55.57	65.90	12.7	25.84	20.87
2750	56.56	67.12	12.9	29.04	23.58
3000	57.49	68.25	13.1	32.30	26.33

These entries were computed by the same formulae and with the same spectroscopic and universal constants as were the numbers below 1500°. It is rather difficult to make estimates of the probable error; it seems likely, however, that even for 3000°, a free energy based on these numbers will be reliable to 300 cal. or so, and that $(E-E_0°)$ will not be in error by more than half a kilocalorie. These data at least possess the advantage of being numerically consistent with those for lower temperatures, and should serve for making rough estimates of equilibrium constants, etc., in this range.

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July 17, 1934.

[1] A. R. Gordon, J. Chem. Phys. **2**, 65 (1934).